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VALUE MAXIMIZATION OF OLEFINIC NAPHTHA

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 28 September, 2014.

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Abstract of master's thesis

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Abstract

Olefin content of gasoline is limited in gasoline specifications since olefins are considered a source of air pollution. This restricts the use of olefinic naphthas in gasoline blending.

Two processing alternatives for olefin removal, hydrogenation and etherification, were studied for olefinic naphthas, FCC naphtha and synthetic naphtha. Effects of processing were studied by modelling hydrogenation with a kinetic model and etherification with a conversion model. Properties of feed and products were estimated with composition based models.

Hydrogenation product suitability for further processing in catalytic reforming was studied. Any of the studied naphthas did not seem to be optimal to catalytic reforming, but some suitable fractions were also found. Possibility to transport the products in Colonial Pipeline was also studied by comparing naphtha properties with Colonial Pipeline's specifications.

Monetary value of processed naphthas and especially the value increase gained by processing were studied with product value estimation methods, which included product comparison to Colonial Pipeline product prices and value estimation with a blending pool model. Also the initial investment costs of processing alternatives were estimated. Difficulties with product value estimation accuracy were encountered, but general conclusion was made that full or partial hydrogenation process did not seem to be profitable investments while etherification and combination of etherification and hydrogenation seemed very promising alternatives. Further studies with the last mentioned processes and better value estimation method was suggested.

Keywords Olefinic Naphtha, Etherification, Hydrogenation, Value Maximization, Synthetic Naphtha, FCC Naphtha

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Tiivistelmä

Bensiinin olefiinipitoisuttaa rajoitetaan bensiinispesifikaatioissa, sillä olefiineja pidetään eräänä ilmansaasteiden aiheuttajista. Nämä rajoitukset vaikeuttavat olefiinisten naftojen käyttöä bensiinin valmistuksessa.

Tässä työssä tutkittiin kahta vaihtoehtoista prosessia, hydrausta ja eetteröintiä, olefiinisen FCC naftan ja synteettisen naftan käsittelyyn olefiinien vähentämiseksi. Käsittelyn vaikutusta tutkittiin mallintamalla hydrausta ja eetteröintiä kineettisellä mallilla ja konversiomallilla. Syötön ja lopputuotteiden ominaisuuksia mallinnettiin käyttämällä seoksen koostumukseen perustuvia ominaisuusmalleja.

Hydrattujen tuotteiden sopivuutta katalyyttiseen reformointiin tutkittiin. Yksikään tutkituista naftoista ei osoittautunut optimaaliseksi syötöksi katalyyttiselle reformoinnille, mutta jokseenkin sopivia fraktioitakin löydettiin. Mahdollisuutta kuljettaa olefiinisia naftatuotteita Colonial Pipeline -putkiverkostossa tutkittiin vertaamalla tuotteiden ominaisuuksia kuljetusluokkien spesifikaatioihin.

Prosessoitujen tuotteiden rahallista arvoa ja erityisesti arvon nousua prosessoinnissa tutkittiin vertaamalla naftoja Colonial Pipelinen tuotehintoihin ja arvioimalla tuotearvoa öljynjalostamon bensiinisekoitusmallilla. Myös prosessointivaihtoehtojen alkuinvestointikustannuksia arvioitiin. Tuotteiden arvon määrityksessä havaittiin mahdollisia puutteita käytettyjen menetelmien tarkkuudessa. Kuitenkin saatujen tulosten perusteella voitiin tehdä johtopäätös, että pelkän hydrauksen sisältävät prosessointi vaihtoehdot eivät vaikuttaneet kannattavilta investoinneilta kun taas eetteröinti prosesseille sekä hydrauksen ja eetteröinnin sisältävälle prosessille saatiin erittäin korkeaan kannattavuuteen viittaavia tuloksia. Saatujen tulosten perusteella voitiin suositella lisätutkimuksia viimeisenä mainituille prosesseille luotettavampaa tuotteen arvon määritystä käyttäen.

Avainsanat olefiininen nafta, eetteröinti, hydraus, arvon maksimointi, synteettinen nafta, FCC nafta

Esipuhe

Tämä diplomityö on tehty 11.12.2013 – 28.9.2014 välisenä aikana Neste Jacobs Oy:n palveluksessa Porvoon Kilpilahdessa. Työn valvojana on toiminut professori Ville Alopaeus ja työn ohjaajina ovat toimineet DI Matti Koskinen ja DI Pekka Nurmi. Haluan kiittää heitä kaikkia kärsivällisestä avusta ja ohjauksesta työni aikana.

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Porvoossa 28.9.2014

Tuomo Eskola

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APPLIED PART

Abbreviations

AKI	Anti-knocking index, (RON + MON) / 2
API	American petroleum institute
ASTM	American Society for Testing and Material
bbl	Barrel (1 barrel = 42 US gallons = 158.9873 litres)
BOB	Blendstock for oxygenate blending
CaRFG	California reformulated gasoline
FCC	Fluid catalytic cracking
LSR	Light straight-run naphtha
MON	Motor octane number
MTBE	Methyl tert-butyl ether
MTG	Methanol to gasoline
MTO	Methanol to olefins
MTP	Methanol to propylene
NO_X	Nitrogen oxides
NPV	Net present value
OCP	Olefin cracking process
RFG	Reformulated gasoline
RON	Research octane number
RVP	Reid vapor pressure
TAME	Tert-amyl methyl ether
THpME	Tertiary pentyl methyl ethers
THxME	Tetiary hexyl methyl ethers
TIGAS	Topsoe's improved gasoline synthesis process
WHSV	Weight hourly space velocity
VOC	Volatile organic carbon

LITERATURE PART

1 Introduction

Poor quality of air is an increasing challenge on metropolitan areas worldwide. It may cause severe illnesses, shortened lifespans, and it decreases quality of life in the most densely populated areas in the world. Major factor in poor urban air quality is smog and its prime component ground-level ozone, which is formed in interaction of volatile organic carbon (VOC) vapors and nitrogen oxides (NO_X). NO_X emissions mainly originate from burning of fuels in motor vehicles and industrial facilities, while a significant source of VOC are volatile components of motor gasoline. All VOC compounds do not form ground-level ozone with equal rates. Olefins and other unsaturated hydrocarbon components of gasoline form ozone considerably faster than their paraffin counterparts. (Rizvi 2009, Faiz et al. 1996)

The environmental reasons have led legislators to restrain maximum olefin content in gasoline specifications. Despite air quality concerns related to olefins, they are also important boosters of octane number, the measure of gasoline's capability to restrict detonation or knocking in combustion engine and thereby the power that engine can deliver (Antos et al. 1995). Olefin content limits set technical challenges to fuel producers who need to meet olefin specifications simultaneously with octane number specifications. These circumstances promote demand to reduce olefins from olefin rich gasoline blendstocks with minimal loss in octane number. In modern oil refining the most important source of olefins has traditionally been Fluid Catalytic Cracking (FCC) unit. However, an emerging olefin rich gasoline component is synthetic naphtha.

The concept of synthetic naphtha was invented in 1910's (Bergius 1932), but development of modern production technology for it dates to 1970's and is related to search of alternative gasoline sources during and after the oil crisis (Marcilly 2006). Current renaissance of synthetic naphtha is supported by multiple trends. For example ongoing building boom of synthetic naphtha producing plants in China (Chen 2012) is believed to be connected to China's interest to become less dependent on foreign oil resources and production of synthetic naphtha from renewable biomass resources has been under interest in the United States (Olsbye et al. 2012).

Unwanted olefins in naphthas can be converted to other compounds. Hydrogenation can be used to saturate olefins into paraffins. This process entails challenge of hydrogenating olefins without negatively affecting naphtha properties like octane number, specific gravity etc. This is not just because olefins have high octane number, but also because saturation of olefins may saturate even better octane boosters, aromatics. Another interesting option to reduce olefins is etherification to methyl ethers, which are important oxygenate octane boosters of gasoline. This thesis studies economical and technical feasibility of the mentioned olefin reducing processes for naphthas. The focus is in processing of synthetic naphtha, which is currently a widely discussed topic. FCC naphtha is researched by side as reference in order to get perspective how this traditional olefin rich naphtha resembles and differs from its synthetic relative.

2 Requirements for Properties of Naphtha in Various Uses

Property requirements for synthetic and FCC naphthas in a number of possible uses are studied in this thesis. Specifications of final gasoline blending products, downstream processing units in refining processes, and even intended transportation methods set certain limits to naphtha properties. In this chapter three different limiting specifications are discussed.

Euro 5 (see definition in subchapter 2.1), the latest European gasoline specification, is used in European gasoline markets, but it has or will be also applied in slightly modified versions in most of world countries including China (International Council on Clean Transportation 2014). Euro 5 is one of the most relevant gasoline specifications for this thesis, as it imposes strict limits for lead, sulfur, and olefin contents just a few to mention. Due to its global importance, Euro 5 gasoline is introduced in this chapter.

Catalytic reforming is one of the most important naphtha upgrading processes in oil refining industry. Further upgrading FCC or synthetic naphtha after hydrogenation with catalytic reforming is considered in this work as a possible post-processing alternative. Since certain features of catalytic reforming set strict prerequisites for the feed quality, the requirements as well as basic principles of catalytic reforming process are discussed in this chapter.

Colonial Pipeline is the most important fuel transportation pipeline in the United States. Many limits exist for petroleum product properties carried in it. In order to safely and conveniently operate this pipeline network, Colonial Pipeline Company has set specifications for the products to be carried. Relevant restrictions for naphtha products are discussed in this chapter.

2.1 Euro 5 Gasoline Standard

EN 228:2012 is a European gasoline specification standard. It takes into account a number of EU directives that define quality and composition requirements for gasoline placed on the market in EU countries. (EN Standards 2012) In this work the gasoline that meets the requirements of EN 228:2012 is referred as "Euro 5 gasoline".

Standard EN 228:2012 is based on requirements of European Fuels Directive 98/70/EC (EN Standards 2012). Directive 98/70/EC itself has been lately amended with EU directives 2009/30/EC and 2011/63/EU. New restrictions set by directive 2009/30/EC are the most fundamental changes of Euro 5 gasoline compares to previous gasoline standard. (EN Standards 2008, EN Standards 2012, Directive 98/70/EC, Directive 2009/30/EC, and Commission Directive 2011/63/EU)

EU directive 2009/30/EC, which amends European Fuel Directive and is taken into account in EN 228:2012 standard, aims for achieving air quality level that does not give serious risk or impact to health or environment. It is said to support regulations that limit emissions from light and heavy duty road vehicles and help community to meet its greenhouse gas reduction goals. The directive also obligates EU member states to ensure that gasoline placed on the market complies with specifications that are stated in annexes of the directive. (Directive 2009/30/EC)

Perhaps the most notable modification in Euro 5 gasoline specifications compared to earlier is the decrease of sulfur content maximum limit to 10 wt-ppm. Also the maximum allowed oxygenate contents have been increased from the previous standard. Euro 5 gasoline property specifications relevant in this work have been described in Table 1. The specification is slightly different for E5 and E10 Euro 5 gasolines, Euro 5 subgrades with maximum ethanol content of 5 and 10 vol-% (EN Standards 2012).

Table 1. Euro 5 gasoline specification for E5 and E10 gasoline fundamental in this work are listed in this table.

Property	Unit	Min Limit	Max limit
RON	-	95.0	-
MON	-	85.0	-
Lead content	mg/l	-	5.0
Density (at 15 °C)	kg/m^3	720.0	775.0
Manganese content **until 2013-12-31** **from 2014-01-01**	mg/l	-	 6.0 2.0
Content of hydrocarbon types **Olefins content** **Aromatics content** **Benzene content**	% (V/V)	 - - -	 18.0 35.0 1.00
Oxygen content **For E5** **For E10**	% (m/m)	 - -	 2.7 3.7
Oxygenates content **For E5** **For E10** **- methanol** **- ethanol** **- iso-propyl alcohol** **- iso-butyl alcohol** **tert-butyl alcohol** **ethers (5 or more C atoms)** **other oxygenates**	 % (V/V)	 - - - - - - - -	 For E5 volume bending restricted to 2.7 % (m/m) maximum oxygen content For E10 3.0 10.0 12.0 15.0 15.0 22.0 15.0

(EN Standards 2012)

2.2 Colonial Pipeline

Major petroleum product delivery pipeline, Colonial Pipeline, is located in South Eastern and Eastern parts of the United States. Basic information about the pipeline and its operation principles are discussed and product specifications relevant to this work are examined.

2.2.1 Introduction to Colonial Pipeline

Colonial Pipeline is a pipeline network that carries petroleum products in south coast and east coast areas of the United States and connects refineries and marketing terminals. Main line of the network reaches from Texas to New Jersey and the system has multiple branches. Map of the pipeline network is presented in Figure 1. Colonial Pipeline delivers on average over 100 million gallons of fuels per day including gasoline, kerosene, heating oil and diesel fuel. (Colonial Pipeline Company 2008)

Figure 1. Map of Colonial Pipeline network in south and east coasts of the United States.

(Financial Post 2011)

Petroleum products are carried in Colonial Pipeline in batches. This means that different products are carried in the same pipeline sequentially. Mixing of different products is controlled by using turbulent flow conditions, by having strictly defined specifications for carried products, and by having protocol for treating of sequential product's mixing areas also known as interfaces. (Colonial Pipeline Company 2008)

Colonial Pipeline is a major carrier of petroleum products in the United States. It has also specifications for products allowed to be carried in the pipeline network. These specifications are relevant for this work, since Colonial Pipeline is considered as possible delivery channel for the naphtha types studied in this thesis.

2.2.2 Product Specifications in Colonial Pipeline

Colonial Pipeline has product specifications for almost one hundred different products including bio-diesels, conventional diesels, kerosenes, fuel oils, reformulated gasolines, conventional gasolines, and gasoline blendstocks (Colonial Pipeline Company 2013). FCC naphtha and synthetic naphtha do not fulfill requirements of ready gasoline products. Therefore only the gasoline bendstocks product category is considered in this work.

Colonial Pipeline Company's product specification recognizes seven blendstock grades. These are known as A, D, F, H, L, S, and T grades. L grade seems to be a somewhat multipurpose grade that sets the minimum requirements for blendstocks that are allowed to be transported in the pipeline. L grade has very wide property limits and it is not recognized in price statistics publications from Argusmedia (a major price publisher of fuel and oil markets in the US). Rests of the grades specify standardized blendstock products that have steady markets. In that sense it is plausible that if blendstock can be transported as one of the latter grades, finding market and good price for the blendstock product becomes much simpler. (Colonial Pipeline Company 2013, Argusmedia 2010)

The least restrictive of Colonial Pipeline Company's product specifications, the L -Grade blendstocks obligates the shipper to supply some basic information about the gasoline blendstock, to test number of blendstock properties and to meet a number of minimum and maximum property limits. Also interface cutting rules for certain gasoline blendstocks are determined. The L-Grade product specification states that shipper must supply to the best of their knowledge the information of gasoline blendstocks octane number, oxygen content, Reid vapor pressure, and any other product property that does not meet Colonial Pipeline Company's specification for 87 octane conventional gasoline (M-Grade). Minimum and/or maximum property limits and correct test methods are specified for gravity, benzene volume percent, Nace corrosion, and Reid vapor pressure. Only test method and obligation to report the result are stated for sulfur content. Property limits and test methods are listed in Table 2. Gasoline blendstock that has anti-knocking index (AKI) lower than 83 is treated with special protocol in order to protect other batches in the pipeline. This means that all interfaces (batch mixing areas) of very low octane blendstock are combined with low octane blendstock batch. Also a special

buffer batch is required to be shipped with the low octane grade. (Colonial Pipeline Company 2013)

Table 2. Colonial Pipeline Company's gasoline blendstock property limits and correct test methods are described in this table.

Product Property	ASTM Test Method	Minimum Test Result	Maximum Test Result
Gravity °API at 60 °F	D287. D1298. D4052	48	80
Benzene (vol %)	D3606		3.8
Nace Corrosion	TM0172	B+ (origin)	
Sulfur (ppmwt)	D2622 or equivalent		Report
RVP (psi)	D5191	4.0	

(Colonial Pipeline Company 2013)

Other blendstock specifications (A, D, F, H, S, and T grades) set stricter limits on many properties. For example these grades may not contain oxygenates, octane numbers have minimum values, and in some cases sulfur, olefin, and aromatics contents are limited. The most essential of these limits are compiled into APPENDIX 1.

2.3 Requirements for Naphtha Properties in Catalytic Reforming Feed

Catalytic reforming in oil refining is a process that produces high octane reformate for gasoline production. The formed benzene, toluene, and xylene components have also petrochemical uses as feed materials (Antos et al. 1995). However, this subchapter is focused on gasoline related reformate production.

Catalytic reforming is typically performed at 3.5–35 bar pressure and 725–800 K temperature in commercial units. Catalyst is typically combination of multiple active components. (Antos et al. 1995) Several catalytic reactions have been identified to occur in catalytic reforming process. These include isomerization, dehydrogenation, and dehydrocyclization reactions where in high octane number iso-paraffins and aromatics are formed. (Surinder 2013) Typically the feed of a catalytic reformer unit is heavy straight-run naphtha containing paraffins, naphthenes and aromatics (Surinder 2013, Digital Refining 2010). Heavy straight-run naphtha is a crude oil fraction consisting of C6 to C12 hydrocarbons with boiling range of 65 to 230 °C. According Digital Refining (2010) non-straight-run naphthas, such as FCC naphtha, can also be processed in a catalytic reformer, but only after intense hydrotreatment.

Feed quality of catalytic reformer has some technical and economical restrictions. Catalyst poisons reduce activity of catalytic processes. Surinder (2013) mentions sulfur and nitrogen as catalyst poisons for catalytic reforming. Mall (2013) extends the list with halogens, oxygen, water, olefins, diolefins, arsenic and other metals. Apart from catalyst poisoning Zhou and Baars (2010) also mention that nitrogen could cause corrosion problems in catalytic reformer by forming ammonium chloride. The preferred feedstocks for catalytic reforming in gasoline production are C7–C9 (Digital Refining 2010) and C7–C10 (Fahim et al. 2010) naphtha cuts. C6 hydrocarbons are avoided since they are benzene precursors and benzene in gasoline is tightly restricted because of its carcinogenic nature. Another reason to C6 avoidance is related to C6 naphthenes. Uniquely cyclohexane and methylcyclopentane both have higher octane number than C6 aromatic benzene, so conversion is not beneficial (Antos et al. 1995). Preferred molecule types in feed are n-paraffins and naphthenes (Fahim et al. 2010) that react forming higher octane number molecules, i-paraffins and aromatics. Industrial practice is that olefins are hydrogenated from feed before catalytic reforming (Mall 2013). High aromatics content makes catalytic reforming useless since feed octane number cannot be effectively increased any more. According to Fahim et al. (2010) preferred content of aromatics in catalytic reforming feed is below 20 vol-%.

3 Synthetic Naphtha Production and Properties

Aim of this chapter is to introduce the concept of synthetic naphtha production and to further discuss its properties. Since value maximization of synthetic naphtha is one of this work's research subjects, its properties and manufacturing are important to discuss.

3.1 Overview of Synthetic Naphtha Production from Methanol

When oil crisis increased raw oil price in the 1970's, alternative sources of gasoline were sought. During this period the concept of using natural coal or gas based methanol to produce hydrocarbons (including gasoline grade naphtha) became a field of interest. (Marcilly 2006) According to Olsbye et al. (2012) bench-scale and pilot-scale demonstrations of methanol-to-gasoline (MTG) process with HZSM-5 catalyst were executed in 1970's and early 1980's. First commercial process started in New Zealand 1985, but was shut down in middle of 1990's due to low crude oil prices. Another synthetic naphtha process called TIGAS process was first demonstrated in 1980's.

(Olsbye et al. 2012) However, no references of commercial production with TIGAS process could be found from literature and are likely not to exist, as only a demo unit is mentioned in Haldor Topsøe's (2014) marketing materials. Basic concepts of MTG and TIGAS are illustrated in Figure 2.

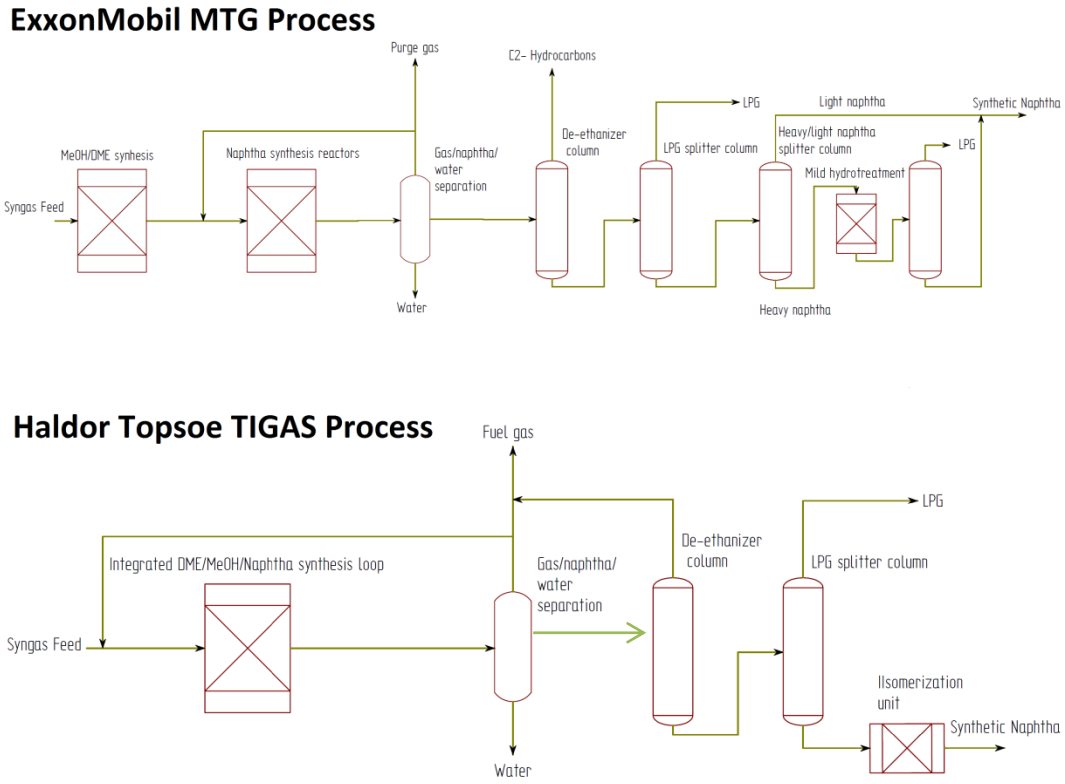


Figure 2. The basic concepts of ExxonMobil MTG and TIGAS processes based on description of ExxonMobil (2014), Haldor Topsoe (2014) and Olsbye et al. (2012). Major differences between the processes are that TIGAS process has according to Olsbye et al. (2012) further integrated reaction steps and less complex separation configuration than MTG process.

By further developing the original MTG concept, similar processes favoring other hydrocarbon products than gasoline grade naphtha have been invented. By adjusting selectivity of used catalyst, methanol to hydrocarbons process can be modified to produce more light olefins or more naphtha including aromatics. (Marcilly, 2006) Discovery of H-SAPO-34 catalyst led to development of Methanol-to-Olefins (MTO) process which favors ethylene and propylene products instead of naphtha. Another

development branch from MTG was a process where highly siliceous HZSM-5 was used. This process is particularly selective to propene and is known as Methanol-to-Propylene (MTP) process. (Olsbye et al. 2012) The essential feature is that MTO and MTP processes produce synthetic naphtha as side products, which makes them highly interesting for this work. Basic concepts of MTO and MTG processes are illustrated in Figure 3.

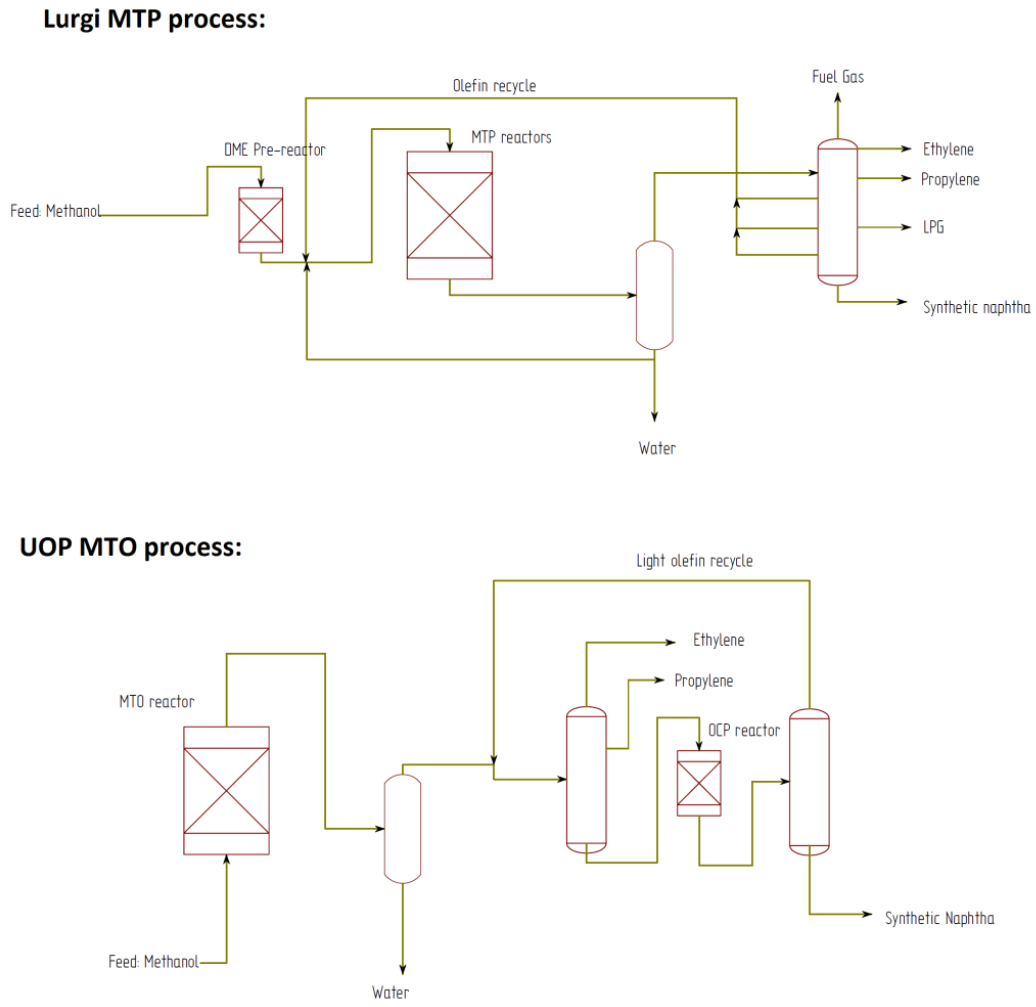


Figure 3. Basic concepts of MTP and MTO processes based on Lurgi (2014) and UOP (2013) description. UOP MTO process contains olefin cracking process (OCP) that increases light olefin yield.

Recent activity in the field of methanol to hydrocarbons processes has been reported from China, where according to Chen et al. (2012) three demonstration processes of coal to olefins processes have already been built and nine others projects were expected

to start soon. Also announcement of TIGAS process demonstration in the USA exploiting biomass gasification has been mentioned by Olsbye et al. (2012).

3.2 Synthetic Naphtha Properties

Some important properties of synthetic naphtha related to modern gasoline regulations are discussed in this chapter. Also its chemical composition is considered. As discussed earlier, multiple naphtha synthesis processes exist. However, information of product properties and compositions are rare in literature. Some rough features of two synthetic naphthas were presented by Phillips et al. (2011), Scheiner (1978) and Rothaemel (2011) and these are summarized in Table 3.

Table 3. Properties and composition of two synthetic naphthas.

Property	**MTP synthetic naphtha**	**MTG synthetic naphtha**
Octane number	-	RON 90 to 100
Carbon number of molecules	more than 5 carbon atoms	10 or less carbon atoms
Paraffin content	Heavy fraction 18.5 wt-% and light fraction 32.6 wt-% paraffins	51 % branched paraffins
Olefin content	Heavy fraction 19.2 wt-% and light fraction 52.9 wt-% olefins	13 % highly branched olefins
Naphthene content	Heavy fraction 19.2 wt-% and light fraction 14.3 wt-% naphthenes	8 % naphthenes
Aromatics content	Heavy fraction 42.4 wt-% and light fraction 0.2 wt-% aromatics	28 % aromatics

(Phillips et al. 2011 Scheiner 1978, Rothaemel 2011)

Phillips et al. (2011) and Scheiner (1978) state the following for MTG process naphtha composition and properties: 51% branched paraffins, 13% highly branched olefins, 8% naphthenes, 28% aromatics, and no oxygenates, RON between 90 and 100, and compound carbon number not greater than 10. This indicates that naphtha from MTG process is chemically rather conventional gasoline grade naphtha with medium olefin content. Based on this information MTG naphtha could be suitable for use in gasoline blending pool without significant processing, since it is not highly olefinic compared to gasoline specifications.

Rothaemel (2011) describes an MTP process. The composition of naphtha product streams are described as following: C7+ hydrocarbons consist of 18.5 wt-% of paraffins, 42.4 wt-% of aromatics, 18.7 wt-% of naphthenes, and 19.2 wt-% of olefins, while C5–C6

hydrocarbons consist of 32.6 wt-% of paraffins, 0.2 wt-% of aromatics, 14.3 wt-% naphthenes, and 52.9 wt-% of olefins. This product has significant olefin content and can be rightly called olefinic. In order to blend this type of naphtha product into gasoline blending pool in large quantities, reduction of olefin content could be necessary to meet gasoline specifications.

4 Properties of Naphtha from Fluid Catalytic Cracking (FCC)

Maximization of FCC naphtha value is studied in this work. In order to do this, it is essential to understand what type of products can be produced with FCC process. That is why compositions and properties of FCC naphtha are discussed in this chapter. The basic process concept of FCC process is also introduced in this chapter.

4.1 Introduction to Fluid Catalytic Cracking Process

Fluid catalytic cracking process is an oil refining process that converts oil fractions to lighter products. A heavy crude oil fraction called gas oil is converted to valuable precursors of transportation fuels such as gasoline, jet fuel, and diesel. Chemical conversion of gas oil is based on catalytic reactions. These reactions are catalyzed with small spherical catalyst particles that are fluidized in a FCC unit. (Sadeghbeigi 2012)

FCC is an important process for refinery's competitiveness. This is due to the fact that significant part of oil refineries gasoline production is based on FCC. FCC unit improves feed value since it converts low value oil fraction into valuable transportation fuels. (Sadeghbeigi 2012)

4.2 Properties of FCC Naphtha

Compared to gasoline specifications, typical FCC naphtha has some special features. These include often large sulfur content and tendency to contain high portion of olefins.

FCC naphtha has typically significantly high sulfur content (Brunet et al. 2005). According to Brunet et al. (2005) this is partly because sulfur containing compounds of crude oil usually have quite high boiling point and therefore end up into FCC unit's gas oil feedstock. Also presence or lack of upstream hydrotreatment impacts FCC naphtha sulfur content. (Brunet et al. 2005)

In order to produce low-sulfur gasoline products from gas oil with FCC, some kind of desulfurization step is usually eventually needed. Depending on refinery, this step can exist before or after the FCC unit. (Ali and Nadhir 2004) Shorey et al. (1999) and Brunet et al. (2005) mention that besides processing gas oil before desulfurization, sulfur content of FCC naphtha can be reduced by adjusting the fractionation of FCC naphtha so that the heaviest 20 percent of gasoline grade naphtha fraction is left out of FCC naphtha. Therefore sulfur content of FCC naphtha can vary depending on earlier refining steps and separation choices.

FCC naphtha is known to often have relatively high olefin contents. For example Brunet et al. (2004) mention that FCC naphtha's olefin content can range from 20 to 40 wt-% and Fan et al. (2009) state that in China and other Asian countries olefin content of FCC naphtha is as high as 40 to 50 %. Olefins provide high octane number and therefore higher value to naphtha. However legislation sets a limit to gasoline's maximum olefin content. For example European standard EN 228 (2012) sets olefin content limit to 18 vol-% and China V standard (currently effective in Beijing and Shanghai) to 24 vol-% (International Council on Clean Transportation 2014, TransportPolicy.net 2014). Ultimate example is Californian CaRFG gasoline that has maximum olefin content of 6 vol-% (Californian Code of Regulations Section 2250-2273.5 2012). These limits are largely lower than FCC naphtha's typical olefin content range of 20 – 40 wt-% mentioned by Brunet et al. (2004) or 40 to 50 % mentioned by Fan et al. (2009). The evident conflict means that in order to meet the demands of latest standards of gasoline products, FCC naphtha must either be processed to lower its olefin content or seriously diluted with other blending components. According to Fan et al. (2009) especially in China approximately 70 % of commercial gasoline is FCC naphtha. In such case blending non-olefinic material alone is not likely to be a viable way for meeting olefin content limits. As one solution Fan et al. (2009) mention possibility to purposely lower the olefin content of gasoline with hydrogenation.

In order to estimate value determining properties of FCC naphtha after hydrogenation, initial composition is required to be identified in detailed level. For this purpose example compositions of FCC naphthas were sought from literature. While general level composition data such as PONA analysis results were easy to find, detailed composition analyses were noted to be rare. The most detailed publically available FCC naphtha

composition was found from Viswanadham et al. (2007) study where composition of FCC naphtha was described in component group and carbon number level. This data is presented in Table 4.

Table 4. Hydrocarbon composition in weight percent of FCC naphtha from an Indian refinery are presented in this table. The density of naphtha was reported to be 0.7142 g/cm^3 (unit assumed), RON 86.0, and sulfur content 1070.7 ppm.

HYDROCARBON	n-paraffin (wt-%)	i-paraffin (wt-%)	Olefin (wt%)	Naphthenes (wt-%)	Aromatics (wt-%)
TOTAL	4.2	38.8	30.3	12.6	13.0
C3	-	-	-	-	-
C4	-	11.8	0.1	-	-
C5	1.5	10.6	12.5	-	-
C6	1.2	5.8	8.7	2.1	0.6
C7	0.5	4.8	7.7	3.7	3.0
C8	0.7	4.1	0.7	5.2	6.5
C9	0.2	1.6	0.5	1.5	2.6
C10	0.1	0.1	0.1	0.1	0.2
C11	-	-	-	-	0.1

(Viswandham et al. 2007)

5 Comparison of Synthetic Naphtha and FCC Naphtha Properties

Finding literature information about typical characteristics of synthetic naphtha or FCC naphtha was found to be difficult. Partial reason for this could be that neither of the naphtha types has very constant properties. As chapter 3 shows, synthetic naphtha's molecular composition can vary widely depending on process. On the other hand gasoline grade FCC naphtha is a distillation cut of wider range of products. Therefore composition of the naphtha fraction depends on how cutting points are selected. Also conditions in FCC reactor and selection of catalyst affect composition of naphtha product. In other words, both naphtha groups are broad collections of diverse naphthas. At least partly of these reasons it is hard (or impossible) to find very specific definition of synthetic naphtha's or FCC naphtha's typical features in literature. Despite that the naphtha groups are heterogeneous, synthetic and FCC naphtha properties are briefly compared with each other in this chapter.

Findings presented in chapters 3 and 4 indicated many similarities but also some differences between synthetic and FCC naphtha. Both products seem to be rich in olefins and poor with n-paraffins. These features clearly differentiate these from typical straight-run naphtha (Ali et al. 2007). It is also distinctive for the products that both have moderate octane numbers (neither is significant octane booster or demoter in gasoline). Naphtha types have similarly carbon number in range of typical gasoline average carbon number. On the other hand notable difference between them is that FCC naphthas have characteristically high sulfur content while synthetic naphthas are sulfur free.

The evident similarity between FCC and synthetic naphtha makes studying value maximization of these products simultaneously justifiable. Their properties can be modified by similar processing steps and comparing widely exploited FCC naphthas to synthetic naphthas in processing scenarios gives reference on how synthetic naphthas can be utilized.

6 Hydrogenation Process as Quality Improvement Method for Olefinic Naphtha

Hydrotreating is a common method in oil refineries for FCC naphtha treatment. As mentioned in previous chapter, FCC naphtha is often hydrotreated in order to remove sulfur. This chapter discusses this conventional purpose of hydrotreatment, but also olefin and aromatics content control of naphtha with hydrogenation. In context of synthetic naphtha olefin and aromatics control can be seen as especially meaningful since sulfur is typically completely absent from it.

6.1 Hydrogenation Process Operation Principle

Hydrogenation in oil refining is a process in which oil fraction is treated with high pressure hydrogen in presence of a solid catalyst. The process can be exploited to gain various effects in oil fractions. According to Audibert (2006) these include removal of sulfur, nitrogen, or metals, hydrogenation of olefinic and aromatic compounds, and hydroconversion reactions where the aim is to modify structure of hydrocarbons by cracking and isomerization. (Audibert 2006)

According to Audibert (2006) catalysts typically used for hydrogenation consist of cobalt-molybdenum (Co-Mo), nickel-molybdenum (Ni-Mo), or nickel-tungsten (Ni-W) active

phase with aluminum oxide (alumina) carrier. Ali and Al-Baghli (2004) state that in case of FCC naphtha desulfurization typical catalysts are Co-Mo/Alumina and Ni-Mo/Alumina, but also that adjusted versions of traditional catalysts have been studied. These adjustments include adding HZSM-5, hydrotalcite and TiO_2 to alumina carrier and introducing alkaline earth and metal oxide to catalyst (Ali and Al-Baghli 2004).

Selective hydrogenation of olefins in olefin-rich naphtha is studied in this work. In case of selective hydrogenation, where maintaining naphtha octane number while meeting product requirements is essential, special requirements for catalyst arise. According to Rase (2000) recommended catalysts for olefin hydrogenation are nickel and noble metal catalysts palladium and platinum. In case of selective olefin hydrogenation in presence of aromatics Rase (2000) mentions palladium as the preferred catalyst choice.

6.2 Naphtha Quality Improvement with Hydrogenation

Hydrogenation is a commonly used post-treatment method for FCC naphtha's desulfurization (Ali and Al-Baghil 2004). As discussed in chapter 4, sulfur reduction of FCC naphtha is often necessary in order to meet legislation defined maximum sulfur content of gasoline.

For sulfur removal purposes, many commercial and licensed hydrogenation technologies exist including OCTGAIN, Prime-G+, SCANfining and CDHydro/CDHDS just few to mention (Ali and Al-Baghi 2004, Bloch 2006). These technologies are almost without exceptions promoted with claims of maximal sulfur removal with minimal loss of octane number. Octane number is typically maintained by avoiding olefin saturation. This olefin sustaining approach is not necessarily the optimal one for olefin-rich naphtha. In fact this work attempts to study hydrogenation cases where saturation of olefins is desired in order to meet requirements of legislation. However, hydrogenation applications for simultaneous olefin reduction and octane number upkeep were noticed to be less discussed in the literature.

Controlling FCC naphtha's sulfur and aromatics content together with olefin content was studied by Viswanadham et al. (2007), who conducted experiments of FCC naphtha hydrogenation with two phase catalytic system. The investigated process concept included first hydrodesulfurization step with Ni-Mo/Alumina and Co-Mo/Alumina catalyst and second hydrogenation step with platinum catalyst. FCC naphtha was

fractionated to heavy (72 wt-%) and light (28 wt-%) fractions and hydrogenation steps were conducted to the heavy fraction. Sulfur in light fraction was reduced separately with Merox extraction, which is a catalytic process where in mercaptan sulfur is reduced by oxidation (UOP 2014). This was done in order to protect olefin rich light fraction from excess olefin saturation in hydrogenation. After processing steps light and heavy fractions were blended. (Viswanadham et al. 2007) Results of the study could be described somewhat promising since olefin content in the naphtha was decreased without loss in octane numbers. The octane loss from olefin and aromatics saturation was compensated by formation of i-paraffins (Viswanadham et al. 2007).

A series of FCC naphtha olefin control related articles have been written by Fan et al. (2005, 2007, 2009a, 2009b, and 2013). In these articles suitable catalysts (Fal et al. 2005 and 2007) and kinetics (Fan et al. 2009a, 2009b and 2013) for FCC naphtha hydrogenation and olefin reduction have been discussed. Fan et al. (2009a) also presented kinetic model for hydrogenation system in which olefins are hydrogenated with Ni-Mo/HZSM-5 catalyst. The subject of the studies was lowering of FCC naphtha olefin content simultaneously with octane number preservation. On negative side this process does not seem to be close to commercialization and it operates in reasonably high 600–700 K temperature.

Any commercialized process concept for combined olefin reduction and octane number retention was not found from literature. If such technologies have not been commercialized (as it seems) successful development of such process could provide good business opportunities.

7 Kinetics for Hydrogenation of Olefinic Naphtha

Naphtha value maximization with a simulation model that contains a hydrogenation step is studied later in the applied part of this thesis. In order to execute these studies, a suitable kinetic model was needed. The aim was to find applicable literature data for kinetic modeling of hydrogenation. This chapter discusses the subject of modelling complex chemical system kinetics and presents the kinetics and kinetic models of hydrogenation that were found from literature sources.

7.1 Kinetic Modelling of Complex Reaction Systems

Kinetic model of a chemical reaction describes mathematically the dependencies of reaction rates. Modeling the kinetics of a fairly simple chemical system typically requires a large amount of empirical data. When considering chemically very complex reaction systems, such as reaction mixtures in petroleum refinery, the task becomes even more difficult. Refinery naphtha consists of numerous light and heavy chemical substances that react with different rates and reaction mechanisms. In this work hydrogenation of two complex mixtures, FCC naphtha and synthetic naphtha, are considered. Ho (2008) describes a few methods for modelling large scale reaction systems. These include traditional partition-based lumping method and total lumping method and more modern methods called composition-based modelling methods (Ho 2008).

Partition-based lumping descends from times when refinery naphtha was typically characterized by examining only basic properties such as specific gravity, average molecular weight, boiling range, and solubility. The composition of naphtha was often examined only on general level. This typically meant using methods such as PONA analysis that divides complex molecular composition to four lumps: paraffins, olefins, naphthenes, and aromatics. Partition-based lumping kinetic models treat complex chemical mixture as lumps or pseudo-components that are easy to classify with simple measurable properties such as boiling point. Partition-based lumping model handles the kinetics of pseudo-component lumps, such as boiling fractions of naphtha. Reaction rates are defined for pseudo-components (lumps) instead of real components. (Ho 2008)

Total lumping is another traditional method for modelling large scale reaction systems. In this procedure all reactants are modeled as a single lump independent of reactant similarities in physical or chemical properties. The aim of this approach is to encapsulate the set of chemical compounds with their individual reactions and kinetics into a single overall kinetics of the whole system. (Ho 2008)

Composition-based modelling methods are a group of more sophisticated methods for kinetic modelling. With novel advanced computational and analytical technologies it is possible to perform detailed analysis of complex mixtures and process the data computationally far better than it was possible a couple of decades ago. Composition-

based modelling uses bottom-up approach. Compositions of mixtures and reactions of compounds or functional groups are analyzed and after the small scale behavior of the system is understood, the lumping is conducted to the system based on understanding of the small scale behavior. (Ho 2008)

7.2 Kinetics of Hydrogenation in Literature

This subchapter discusses the hydrogenation kinetics and kinetic models of naphtha components and kinetic models of complex naphtha mixtures found from literature. Especially hydrogenation kinetics in presence of noble metal catalyst were sought. In order to understand naphtha hydrogenation, reactions of olefins and aromatics were considered relevant. This is because saturation of olefins was the objective, but loss of aromatics would seriously reduce octane number of naphtha. According to Rase (2000), hundreds of studies for individual hydrocarbon compound reactions exist, but studies of complex feedstocks, such as naphthas, are rare in literature. This view is in line with observations made in this literature survey.

According to Rase (2000), selection of hydrogenation catalyst has a significant impact on selectivity. As mentioned in chapter 6, Rase (2000) states that the typical catalysts for olefin hydrogenation are palladium, platinum, and nickel catalysts and for selective hydrogenation of olefins in presence of aromatics, the suggested catalyst is palladium. Other parameters besides the selected catalyst that affect the selectivity of the hydrogenation include hydrogen partial pressure, temperature, additives, metal loading, and pore diffusion (Rase 2000).

Seemingly comprehensive review of sulfur compound hydrogenation in literature has been published by Girgis and Gates (1991), but none of the studies mentioned were conducted in presence of noble metal catalysts. Girgis and Gates (1991) have also listed and reviewed aromatics hydrogenation kinetic studies in presence of non-noble metal catalysts. Kinetics and kinetic models of various aromatics hydrogenation in presence of nickel catalyst have been studied and determined by Rantakylä et al. (1996) and Toppinen et al. (1996a, 1996b).

Fan et al. (2009a) described a six-lump kinetic model for FCC naphtha hydroconversion. Reaction system for the kinetic model uses Ni-Mo active metal catalyst with steam/citric acid modified HZSM-5 as support. The model divides FCC naphtha into six lumps that are

n-paraffin + naphthene lump, i-paraffin lump, n-olefin lump, i-olefin lump, cyclo-olefin lump, and aromatics lump. The lumps and reactions are presented in Figure 4. The model assumes all reactions are of first-order and irreversible. Reaction rates were experimentally measured in four different temperatures and reaction rate constants were calculated with linear regression. Study of the effect of space velocity and operation pressure into reaction kinetics was included in the model. (Fan et al. 2009a) In Ho (2008) classification this model can be categorized as partition-lump model since kinetics are modelled for coarse lumps based on compound groups. The hydroconversion discussed above is specifically intended for lowering the olefin content of naphtha without significantly lowering the naphtha's octane number.

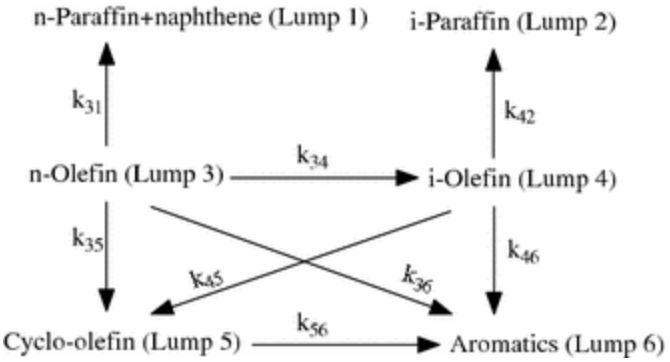


Figure 4. The lumps and directions of irreversible reactions in Fan et al. (2009a) kinetic model are presented in this figure.

(Fan et al. 2009a)

Study of FCC naphtha hydroconversion kinetic model was also conducted by Ocaraza (2004). Experimental studies were carried out with semi-complex mixture that resembled FCC naphtha. Studied catalysts included Alumina + ZSM5, Mo-Alumina + ZSM5, and Pt-Alumina + ZSM5 catalysts. Reactor type was tubular reactor with constant flow. (Ocaraza 2004) The suggested model can be categorized as composition-based model in Ho's (2008) classification since reactions are analyzed on a molecular level but the reaction rate constants are "lumped" to include the following reaction types: dehydrogenation, isomerization, cracking, dimerization-cracking, alkylation, and hydrogenation reactions.

Information that was discovered about selective hydrogenation kinetics from literature was found to be insufficient and/or unsuitable for the needs of this thesis. Hence some

internal unpublished hydrogenation measurement data of Neste Oil was eventually used as the basis for hydrogenation kinetics in the Applied Part.

APPLIED PART

8 Introduction to Applied Part

Applied part of this thesis aims for studying value maximization of FCC naphtha and synthetic naphtha. The naphtha value is studied in process configurations containing hydrogenation step and/or etherification step. Etherification and hydrogenation have an effect on naphtha value since they affect many key properties of fuel naphthas. Whether the net effect on product value is positive or negative may depend on how much and which properties are adjusted and what is the final use of the naphtha.

Four synthetic naphthas and two FCC naphthas were selected as research subjects. Compositions of these mixtures were found from Neste Jacobs internal sources. Value of these mixtures and their hydrogenation and etherification products were researched with indirect and direct methods. The indirect methods included studying the suitability of naphthas for feed of a potential reprocessing alternative catalytic reforming and for transportation in a major transportation pipeline, Colonial Pipeline. The indirect methods did not show direct relation between product value and processing but gave information about some important product features. The direct methods studied directly the costs of processing and the monetary value of products. Unprocessed and hydrogenated/etherificated products values were studied by comparing naphthas to Colonial Pipeline product specifications and prices and by studying the naphtha values in three different refinery blending pool cases. The investment costs were examined by sizing example processes and estimating the investment costs.

In order to specify the research objectives of this thesis, the following research questions were defined:

1. What are properties of FCC naphtha and synthetic naphtha before and after selective hydrogenation and/or etherification of olefins?
2. What are the most suitable fractions of studied mixtures for selective hydrogenation and etherification feed?
3. How do the studied mixtures fit in quality requirements of Colonial Pipeline's or catalytic reforming's feed and how does etherification and hydrogenation affect the suitability?

4. What are the values of studied naphthas in various refinery blending pools with and without selective hydrogenation and/or etherification?
5. What are the investment costs for hydrogenation process, etherification process and a process combining selective hydrogenation and etherification?
6. Is selective hydrogenation and/or etherification of studied naphthas profitable?

9 Specification of the Examined Process System and Calculation Models

This chapter describes the basic concept of the studied process system and key calculation models exploited in this thesis. The models include lumped composition model for the studied mixtures, model for distillation step in the studied process, kinetic model for hydrogenation step, conversion model for etherification step, composition based property models for octane numbers, Reid vapor pressure, and volatility of the studied mixtures, and refinery blending pool model for the evaluation of value of studied mixtures.

9.1 Process Configuration of the Studied System

A simplified process system was selected as research environment. Configuration of this system is presented in Figure 5. The system consists of a distillation step, a hydrogenation step, and an etherification step. The feed is first fractionated into six equal mass fractions that are fed into hydrogenation step, etherification step or bypass. Finally all flows are combined into single product flow. This configuration imitates situation in synthetic naphtha production. Synthetic naphtha is separated from other products with a distillation step (see Figure 2 and Figure 3). Several side draws could be added into this distillation with minor monetary investment and each fraction could be processed differently. Configuration presented in Figure 5 illustrates the system and is intended for studying the profitability of different processing scenarios. Etherification and hydrogenation are parallel and competing processing alternatives in Figure 5 configuration. This setup is justifiable for two reasons:

1. If etherification product would be fed into hydrogenation step, oxygen in etherification product could cause catalyst deactivation. Therefore this alternative is not feasible.

2. The same components react in hydrogenation and etherification. Partial hydrogenation of olefins in hydrogenation step before etherification would drastically lower ether production in etherification step. For this reason this alternative was also found unfit.

Since placing processing steps in series was found unsuitable, parallel configuration was chosen for examination.

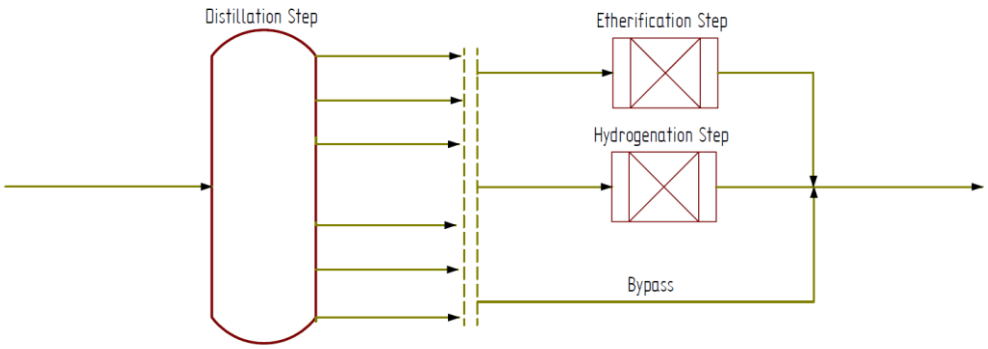


Figure 5. Flow diagram of the studied process configuration.

From utility price and availability point of view, processing configuration is assumed to be located on industrial area where chemical industry raw materials are readily available and connection to transportation pipeline exists. This location scenario is possible or even likely for synthetic naphtha.

9.2 Pseudo-component Composition Model

Composition data of complex naphtha mixtures is often presented in a simplified way using a pseudo-component model. Since available composition data studied in this thesis was partly available in simplified form rather than in actual composition of chemical compounds, it was meaningful to define a pseudo-component interface model that was similar for all studied mixtures. This approach had benefit of allowing definition of pseudo-component properties for the molecular lumps of the model. With pseudo-components properties and suitable property mixing rules, calculation of naphtha properties after separation and processing steps was enabled. Based on available composition data, appropriate lumped composition model was formulated. Each lump was modeled as pseudo-component with properties based on real component. 44

pseudo-components were defined in total. These were selected based on compositions of studied mixtures so that a suitable lump was defined for all components that existed in the mixtures in significant amounts. The calculation of pseudo-component properties is discussed later in this chapter. The lumping of composition model is presented in Table 5.

Table 5. Lumped composition model with 44 lumps. Components are lumped based on substance group and number of carbon atoms.

Carbon no.	Naphthenes	n-Paraffins	i-Paraffins	Cyclo-Olefins	Olefins	Aromatics	Methyl Ethers
3	-	C3-n-paraffins	-	-	-	-	-
4	-	C4-n-paraffins	C4-i-paraffins	-	C4-olefins	-	-
5	C5-naphthenes	C5-n-paraffins	C5-i-paraffins	C5-cyclo-olefins	C5-olefins	-	MTBE
6	C6-naphthenes	C6-n-paraffins	C6-i-paraffins	C6-cyclo-olefins	C6-olefins	C6-aromatics	TAME
7	C7-naphthenes	C7-n-paraffins	C7-i-paraffins	C7-cyclo-olefins	C7-olefins	C7-aromatics	THxME
8	C8-naphthenes	C8-n-paraffins	C8-i-paraffins	C8-cyclo-olefins	C8-olefins	C8-aromatics	THpME
9	C9-naphthenes	C9-n-paraffins	C9-i-paraffins	C9-cyclo-olefins	C9-olefins	C9-aromatics	-
10	C10-naphthenes	C10-n-paraffins	C10-i-paraffins	C10-cyclo-olefins	C10-olefins	C10-aromatics	-
11	-	-	-	-	-	C11-aromatics	-

9.3 Distillation Model

Aspen Plus process simulation program was used for simulating distillation step (see Figure 5). Since Aspen Plus libraries contain limited selection of defined components, simulating distillation of complex mixtures such as naphthas is not straightforward. All necessary real components cannot be found ready defined. Also the exact compositions of studied naphthas were not fully known. These problems were solved by simulating distillation of pseudo-components defined in lumped composition model (see subchapter 9.2).

Simulation of pseudo-components was conducted by selecting suitable real components from Aspen Plus databank (APV73). Thermodynamics of distillation was modeled by using Peng-Robinson equation of state (Peng and Robinson 1976). Distillation mass feed of each pseudo-component was linearly divided into equivalent real components. Multiple real components were used to model each pseudo-component when possible in order to gain smooth compositions in different distillation fractions. In other words by using multiple real components to model one pseudo-component, varying boiling points inside single lump was attempted to replicate. After distillation step the same conversion was analogously used to convert real components of Aspen Plus back to pseudo-components. An example of single lump's conversion to Aspen Plus components and back is illustrated in Figure 6. Complete list of conversions is presented in APPENDIX 2.

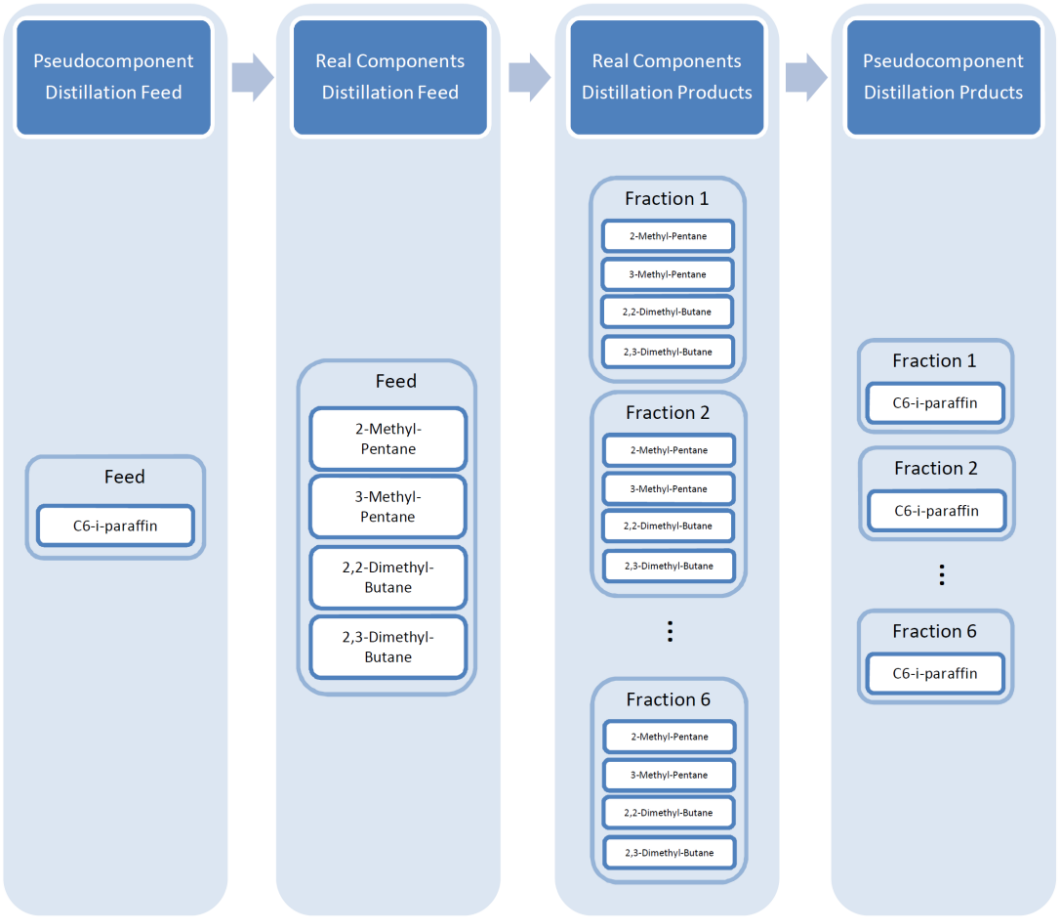


Figure 6. Conversion of C6-i-paraffin pseudo-component to real components and back.

The modelled column contained 13 ideal stages. Feed contained vapor fraction of 0.1 and was fed above column stage 7. The feed and the column were in approximately 0.8 bar absolute pressure which was suitable for assumed utilities (temperature region inside the column is well between condensing temperature of atmospheric water vapor and temperature of natural cooling water (30 °C)). The column's reflux ratio was set to 2.0. Product streams with equal mass flows were located on stages 1, 3, 5, 9, 11, and 13. Draft of distillation column configuration is shown in Figure 7. All the selected column operating parameters were not necessarily optimal from economical point of view, but for calculating the expected compositions of distillation fractions they were considered to be appropriate.

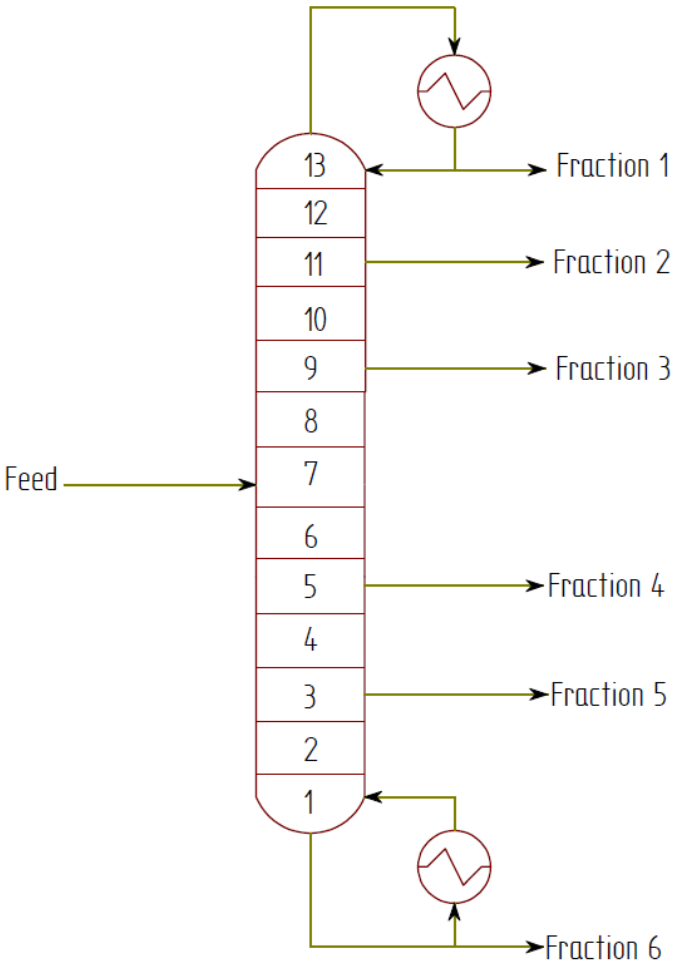


Figure 7. Scheme of the modelled distillation column.

9.4 Kinetic Model for the Hydrogenation

Studying a process for selective hydrogenation of olefins in presence of aromatics, was selected as one of the subjects of this thesis. The target for the hydrogenation is to lower olefin content of feed without saturation of aromatics. In order to study this subject, a kinetic model for selective hydrogenation was needed. Published kinetic models for this type of hydrogenation were not found so the model needed to be constructed from other sources.

Results from an internal hydrogenation experimental program of Neste Oil were used as basis of the kinetic model. Studies of catalytic selective hydrogenation of synthetic naphtha with lab scale plug flow reactor were made in this program. The basic flow

chart of reactor configuration is illustrated in Figure 8. Kinetic model was derived from reactions in 30 bar pressure and 160 °C temperature. The experimental system was operated with 20:1 recirculation ratio. Based on information from the catalyst manufacturer, the active metal of catalyst was very likely palladium. Synthetic naphtha with high olefin and aromatics contents was hydrogenated in the reactor.

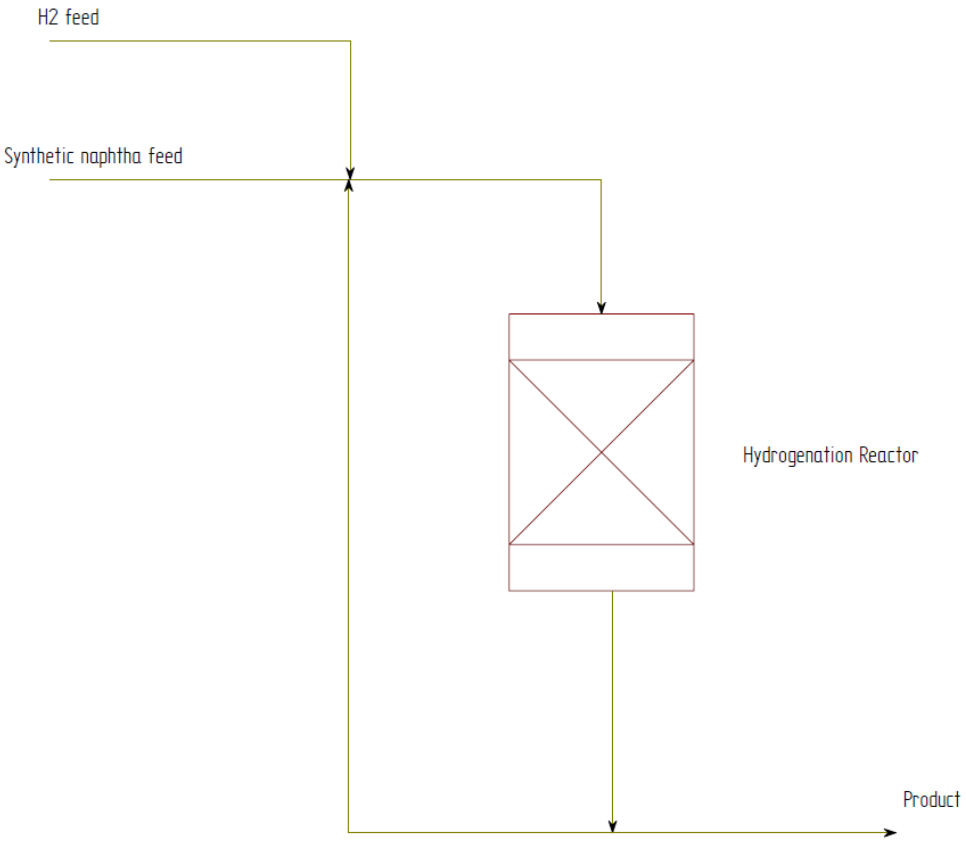


Figure 8. Flow chart of the hydrogenation of synthetic naphtha in Neste Oil hydrogenation study.

Results of the study showed negligible conversion of aromatics and high conversion of olefins, cyclic olefins, and di-olefins. Chemical reactions in the system were estimated based on weight fractions of molecular groups in feed and product. The assumed products of reacting components are presented in Table 6. Because conversion of aromatics in test reactor was low, it was taken as zero in kinetic model. It is notable that the hydrogenation of olefins in test reactor was not complete. Therefore it is possible that conversion of aromatics remained low because olefins dominated active sites of catalyst thus preventing any significant conversion of aromatics. No experimental

evidence of this was available, but there is possibility that if all olefins were hydrogenated, aromatics saturation could rise. That is why conversion of hydrogenation reactor model was restricted so that minimum applicable olefin content in reactor output was 2.5 wt-%.

Table 6. Reacting component and products of occurring hydrogenation reactions. The carbon numbers of molecules are assumed to stay the same in the reactions.

Reacting component	**Product**
n-olefin	n-paraffin
i-olefin	i-paraffin
cyclic olefin	naphthene

Experimental data from Neste Oil hydrogenation study alone was found insufficient for development of a kinetic model. Therefore information about reaction mechanisms and activation energies were sought from the literature. Most applicable data was found from the study by Alexander et al. (2012), which discusses the kinetics of olefin hydrogenation with palladium catalyst. It was found to be an applicable reference, since the active metal was the same as the active metal in Neste Oil's hydrogenation study. Mechanism and reaction rate equation were derived by Alexader et al. (2012) for the hydrogenation of 1-hexene. The mechanism is depicted in Figure 9 and the reaction rate equation is presented in Equation 1. All olefin hydrogenations in Neste Oil's reaction study were assumed to occur with the same mechanism and reaction rate equation. The generalized reaction rate equation for all olefins is presented in Equation 2. Temperature dependencies of the reactions were assumed to obey Arrhenius equation (Equation 3). Equilibrium constants and activation energies of all olefin hydrogenation reactions were assumed to equal equilibrium constant and activation energy of 1-hexene hydrogenation (K = 53.5 and E_a = 41000 J/mol) (Alexander et al. 2012).

$$r = \frac{Kk_1 C_{ctalyst} C_{1-hexene} C_{H2}}{1 + KC_{1-hexene}} \quad (1)$$

Where

r is reaction rate ((mol/dm^3)/s),

K is equilibrium constant of reversible reaction, where 1-hexene bonds with catalyst (first step in Figure 9),

k_1 is reaction rate constant of 1-hexene hydrogenation (second step in Figure 9),

$C_{catalyst}$ is concentration of catalyst (mol/dm^3),

$C_{1\text{-}hexene}$ is concentration of 1-hexene (mol/dm^3), and

C_{H2} is concentration of hydrogen (mol/dm^3).

(Alexander et al. 2012)

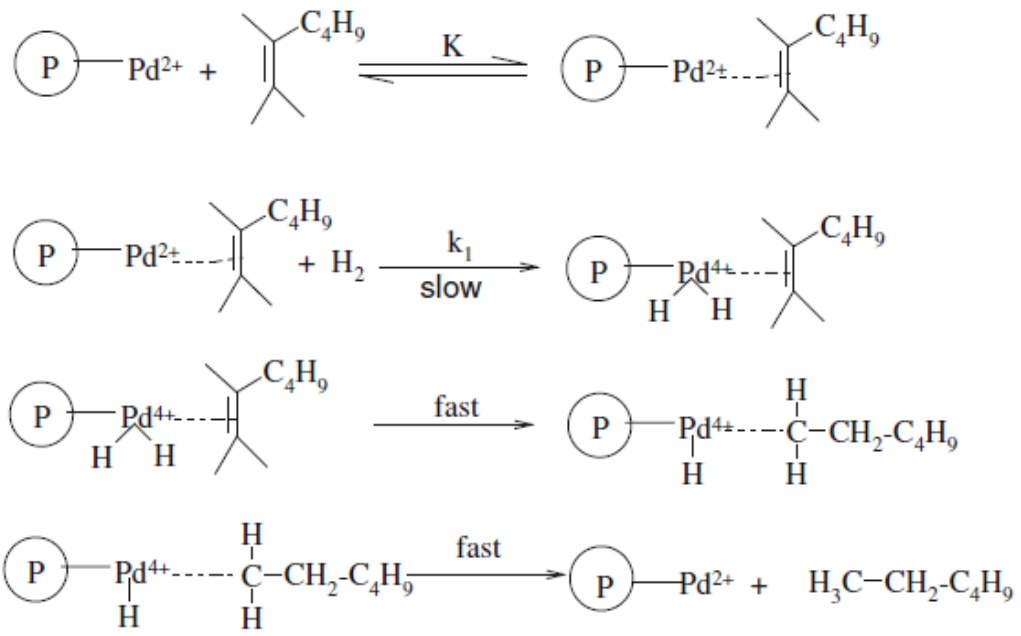


Figure 9. Mechanism of 1-hexene hydrogenation with palladium catalyst.

(Alexander et al. 2012)

$$r = \frac{KkC_{catalyst}C_{olefin}C_{H2}}{1 + KC_{olefin}} \quad (2)$$

$$k = Ae^{\frac{-E_a}{RT}} \quad (3)$$

Where

A is pre-exponential factor

e Euler's number

E_a is the assumed activation energy of the hydrogenation reactions (J/mol),

R is universal gas constant (J/(K·mol),

T is temperature (K),

r is reaction rate ((mol/dm^3)/s),

K is equilibrium constant of reversible reaction, where olefin bonds with catalyst,

k is reaction rate constant of olefin hydrogenation,

$C_{catalyst}$ is concentration of catalyst (mol/dm^3),

C_{olefin} is concentration of olefin (mol/dm^3), and

C_{H2} is concentration of hydrogen (mol/dm^3).

After kinetic model was selected, the model's parameters were defined so that they were consistent with the experimental data from Neste Oil's hydrogenation studies. Concentration of catalyst in Neste Oil's hydrogenation reactor was estimated by calculating empty volume of reactor (based on estimated catalyst porosity) and by assuming the catalyst material palladium content to be 5 wt-%. Composition of product and fresh feed were known since those were reported in Neste Oil's documentation. The composition of reactor feed could be calculated based on known fresh feed content, product content, and recirculation ratio. After this the actual conversion of olefins over reactor once-through could be calculated. Hydrogen concentration in reactor was presumed to stay in saturated state through entire length of reactor. The solubility of hydrogen was estimated by modeling the hydrogenation product mixture with Aspen Plus and feeding the mixture in a flash unit with excess hydrogen in 30 bar absolute pressure and 160 °C temperature. Peng-Robinson with Boston-Mathians alpha function (PR-BM) equation of state was used as the thermodynamic model. The 3 mol-% hydrogen content in liquid product of flash unit was assumed to estimate the solubility of hydrogen in the mixture. Finally the reaction rate constants for hydrogenation reactions were fitted based on experimental data and presumed reaction parameters. The reaction rate constants were determined individually for six molecular classes: C5-C7 cyclo-olefins and C5-C7 i- or n-olefins. Experimental data did not enable determination of rate constants to other carbon number olefins. Hence all components with carbon number lower than 5 were assumed to react with the same rate as C5

components and all components with carbon number higher than 7 were expected to react with the same rate as C7 components.

9.5 Conversion Model for Etherification

Besides hydrogenation, etherification is another processing unit studied for naphtha value maximization in this thesis. The etherification unit converts olefins and methanol into methyl ethers. Methyl ethers are oxygenate components of gasoline that function as octane boosters. Therefore converting olefins in FCC and synthetic naphtha into methyl ethers could increase its value.

Reactions in etherification unit were modeled without kinetic model using only component based conversions. Based on Neste Jacobs' internal knowledge and data, reactivity of certain reactive C4–C7 olefins were assumed. Conversions and reactive compounds of C4–C7 olefins are listed in APPENDIX 5, which shows high (99 and 90 %) conversions for reactive C4 and C5 olefins and moderate (60 %) for C6 reactive olefins and low (25 %) for C7 reactive olefins. Conversions of any heavier olefins were presumably near to zero. Analysis of studied synthetic naphtha and FCC naphtha molecular compositions revealed, that portions of reactive olefins in C4–C7 olefins were similar among studied four synthetic naphthas and among two FCC naphthas, but differed between the two naphtha types. The approximate portions of reactive olefins of C4–C7 olefins in FCC and synthetic naphthas are listed in Table 7. These values were also used for modeling olefin etherification in this thesis. Actual conversions of C4–C7 olefin molecular groups were calculated as product of reactive olefin portions and conversions of reactive olefins (see Equation 4).

$$C_O = x_{RO} C_{RO} \tag{4}$$

Where

C_O is conversion of olefins in molecular group (C4 to C7 olefins),

x_{RO} is portions of reactive olefins in molecular group, and

C_{RO} is conversion of reactive olefins.

Table 7. Portions of reactive olefins (C4–C7) in FCC and synthetic naphthas.

Molecular group:	Portion of reactive olefins of all olefins in synthetic naphthas:	Portion of reactive olefins of all olefins in FCC naphthas:
C4-olefins	40 mol-%	10 mol-%
C5-olefins	65 mol-%	50 mol-%
C6-olefins	63 mol-%	50 mol-%
C7-olefins	60 mol-%	30 mol-%

9.6 Composition Based Property Calculation Models

All models introduced in this subchapter are intended for calculating properties of mixtures based on pure component properties. These models are needed since naphtha properties depend on composition. All the models exploit the composition model introduced in subchapter 9.2. This is meaningful since many properties are unknown to some components, but the general trend within a molecular group can be handled by defining average value for pseudo-components of the composition model.

9.6.1 Octane Number Model

Potentially the most important property to naphtha's value is its octane number. Therefore having a model to estimate this number is essential. The model introduced here is combination of estimating pseudo-component octane numbers and calculating the total octane number of pseudo-component mixture.

First the research octane number (RON) and motor octane number (MON) for the pseudo-components of composition model were determined. Real component octane number data for pseudo-component model was acquired from ASTM (1971) and Ghosh et al. (2006) and for methyl ethers from Chase et al. (1980).

Each n-paraffin pseudo-component consists of only one component and therefore the pseudo-component RON and MON are the same as the RON and MON of the n-paraffin that they represent. Aromatic, naphthene, and cyclic-olefin octane numbers were determined by calculating average of RON and MON available in literature from the components that they represent.

As stated by Ghosh et al. (2006) octane number of i-paraffins is highly dependent on the number of branches in molecular structure. This behavior is illustrated in Figure 10. On the other hand the number of i-paraffin branches tends to vary depending on the type of hydrocarbon mixture. This phenomenon is illustrated in Table 8. Therefore, a more complex calculation method was needed for determination of i-paraffin octane number values. Since olefin pseudo-components of this work include both n-olefins and i-olefins, the phenomenon had to also be taken into account with octane numbers of the olefin pseudo-components.

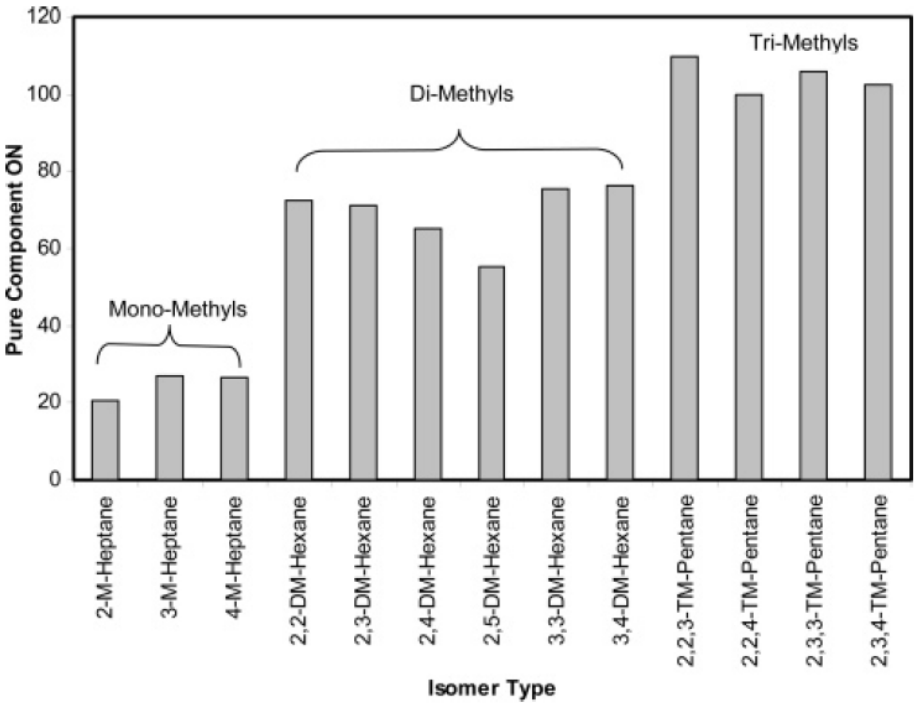


Figure 10. Research octane number's dependency of i-paraffin branch number.

(Ghosh et al. 2006)

Table 8. Fraction of mono-, di-, and trimethy i-paraffins in certain hydrocarbon mixtures (% of all i-paraffins).

Stream type	mono-methyls	di-methyls	tri-methyls
alkylates	0	18.5	81.5
reformates	68.9	31.1	0

(Ghosh et al. 2006)

The branch numbers of i-paraffin and olefin pseudo-components were solved by examining known light fraction compositions of synthetic naphthas 1–4 and FCC naphthas 1–2. Correlation between the carbon number of a component and the number of branches was fitted (heavier molecules have more branches than the light ones) and with the obtained correlation, the number of branches in heavier pseudo-components was estimated. Correlation was derived separately for i-paraffin and olefin pseudo-components for which octane numbers were calculated so that average number of branches in each molecular group was taken into account. The estimated octane numbers of pseudo-components are shown in Table 9 and Table 10. The main point of this procedure was to estimate octane number of i-paraffins and olefins so that average number of branches in the molecules was considered.

Table 9. Estimated research octane numbers (RON) of composition model pseudo-components.

Carbon no.	Naphthenes	n-Paraffins	i-Paraffins	Cyclo-Olefins	Olefins	Aromatics	Methyl Ethers
3	-	97.10	-	-	-	-	-
4	-	93.80	102.00	-	98.70	-	-
5	100.00	61.70	92.30	93.30	94.10	-	118
6	87.15	24.80	81.41	88.75	92.44	102.70	112
7	78.80	0.00	70.04	88.60	83.11	118.00	100
8	55.00	-15.00	56.10	90.30	75.13	112.00	90
9	35.00	-20.00	46.15	90.77	70.29	110.00	-
10	25.00	-30.00	34.75	91.54	65.44	109.00	-
11+	-	-	-	-	-	105.00	-

Table 10. Estimated motor octane numbers (MON) of composition model pseudo-components.

Carbon no.	Naphthenes	n-Paraffins	i-Paraffins	Cyclo-Olefins	Olefins	Aromatics	Methyl Ethers
3	-	97.10	-	-	-	-	-
4	-	89.60	97.60	-	82.15	-	-
5	84.90	62.60	90.30	69.70	80.20	-	101
6	78.60	26.00	79.89	67.95	78.14	105.00	99
7	73.50	0.00	72.90	70.60	73.03	103.50	90
8	50.00	-20.00	62.00	74.23	68.08	101.98	77
9	30.00	-20.00	53.96	77.21	65.14	101.00	-
10	20.00	-30.00	45.10	80.35	62.20	98.00	-
11+	-	-	-	-	-	94.00	-

Second part of this octane number model was calculating the octane numbers of mixture that consists of pseudo-components discussed above. According to Ghosh et al. (2006) due to non-linear interactions between molecular classes, calculating octane number of a mixture as simple volumetric average of component octane numbers is not very accurate. When the linear blending of component's octane numbers was attempted in this work, results that support the view of Ghosh et al. (2006) were achieved. Therefore a nonlinear component based octane blending model from Ghosh et al. (2006) was selected for the prediction of octane numbers of a blend.

Ghosh's et al. (2006) component based octane blending model takes into account the non-ideal interactions between some molecular classes (Ghosh et al. 2006). The key principle of this model is presented with Equations 5 and 6. The parameters for the Equations 5 and 6 are presented in Table 11. Although the model application area with ethers was limited to MTBE and TAME only, in lack of better solutions the model was here applied to heavier ethers as well.

$$ON = \frac{\sum_{PONA} v_i \beta_i ON_i + I_P \sum_P v_i \beta_i ON_i}{\sum_{PONA} v_i \beta_i + I_P (\sum_P v_i \beta_i - \sum_P v_i)} \quad (5)$$

$$I_P = \left(\frac{k_{PN}^{(a)} v_N + k_{PO}^{(a)} v_O}{1 + k_{PN}^{(b)} v_N + k_{PO}^{(b)} v_O} \right) \quad (6)$$

Where,

ON_i is pure component octane number (RON or MON) of component *i*,

Σ_{PONA} is a summation over components belonging to molecular classes paraffin, olefin (including cyclic and non-cyclic), naphthenes, and aromatics,

Σ_P is a summation over components belonging to molecular class paraffin

v_i is volume fraction of component *i*,

β_i is adjustable parameter that determines whether octane number of component *i* in mixture is less than pure component octane number ($\beta < 1$) or higher than pure component octane number ($\beta > 1$),

I_P is interaction term that describes the nonlinear paraffin - naphthene and paraffin - olefin blending interactions,

$k_{PN}^{(a)}$, $k_{PN}^{(b)}$ are adjustable interaction parameters of the model for paraffin - naphthene,

$k_{PO}^{(a)}$, $k_{PO}^{(b)}$ are adjustable interaction parameters of the model for paraffin - olefin, and

v_N, v_O are total volume fractions of naphthene and olefin component class components.

(Ghosh et al. 2006, Ghosh et al. 2009)

Table 11. Parameters for the Ghosh et al. (2006) octane blending model.

Parameter class	Description or applicability	β(RON)	β(MON)
n-paraffins	C_4–C_{12} n-paraffins	2.0559	0.3092
i-paraffins	C_4–C_{12} mono-, di-, and trimethyl-i-paraffins	2.0204	0.4278
naphthenes	C_5–C_9 naphthenes	1.6870	0.2821
aromatics	C_6–C_{12} aromatics	3.3984	0.4773
olefins/cyclic olefins	C_4–C_{12} linear, branched and cyclic olefins	8.9390	10.0000
oxygenates	MTBE, EtOH, TAME	3.9743	2.0727
interaction parameters	$k_{PN}^{(a)}$, $k_{PN}^{(b)}$, $k_{PO}^{(a)}$, $k_{PO}^{(b)}$	0.2, 2.4, 0.4, 3.6	0.2, 2.4, 0.4, 3.6

(Ghosh et al. 2006)

The octane calculation model was verified by comparing predicted octane numbers to measured ones. The comparison showed satisfying results. Estimation of the octane number of two reasonably heavy naphthas led into unaccurate values (see the two data points in bottom-right section of Figure 11), but others estimates were quite close to measured values. Since naphthas studied in this thesis are not very heavy, the

unaccuracy in heavy naphtha octane number estimation was considered insignificant. The results of predicted and measured octane number comparison are shown in Figure 11.

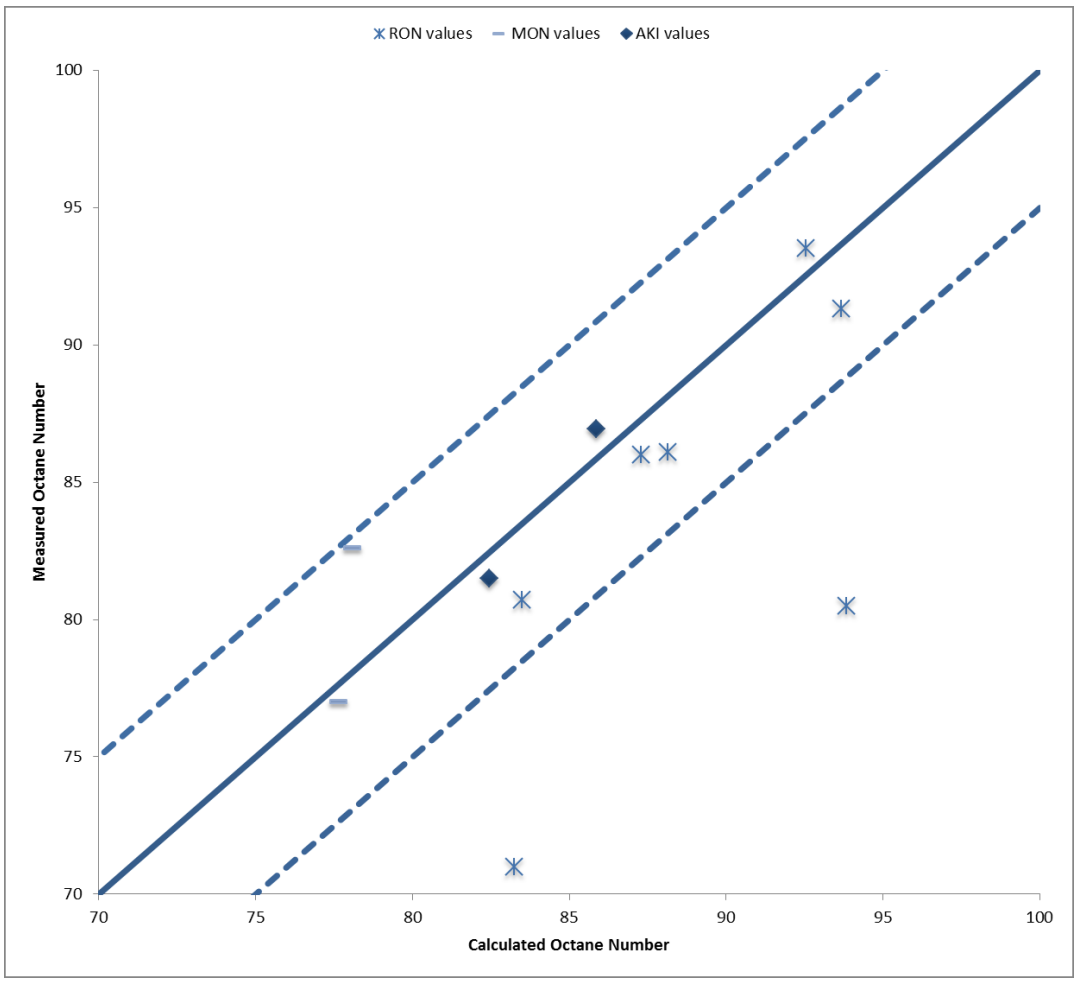


Figure 11. Comparison of measured octane numbers to calculated octane numbers. Dashlines show +/-5 octane number errors. Measured octane numbers and compositions of FCC and synthetic naphtha test mixtures were acquired from Viswanadham et al. (2007) and Neste Jacobs' internal sources.

9.6.2 Reid Vapor Pressure Model

Reid vapor pressure is a standard measure of gasoline's volatility. Reid vapor pressure differs slightly from true vapor pressure. By definition Reid vapor pressure is vapor pressure in presence of air and water vapor at 100 °F temperature (ASTM International Standards 1999). Pure component data was available for true vapor pressure in 100 °F.

To calculate Reid vapor pressure of a mixture, the following calculation method was used:

1. Calculation of true vapor pressure of the mixture in 100 °F based on pseudo-component vapor pressures and
2. Converting the true vapor pressure of the mixture into Reid vapor pressure.

True vapor pressure of each pseudo-component was calculated as an average of the real components that it represents. The vapor pressure data of real components were acquired from ASTM (1971). Pseudo-component vapor pressures based on literature data are presented in Table 12. This table is presented in non-metric units, since both, literature source and TVP-to-RVP conversion equation, were expressed in non-metric units. The true vapor pressure of the mixture was approximated by calculating the partial pressures of the pseudo-components with Raoult's law. The partial pressures of pseudo-components were calculated as product of component's molar fraction and pure component vapor pressures (Equation 7) and vapor pressure of the mixture was calculated by summing the partial pressures of the pseudo-components (Equation 8).

Table 12. Calculated vapor pressures of pseudo-components. Vapor pressures are presented in pounds per square inch (psi) at 100 °F temperature.

Carbon no.	Naphthenes	n-Paraffins	i-Paraffins	Cyclo-Olefins	Olefins	Aromatics	Methyl Ethers
3	-	190.00	-	-	-	-	-
4	-	51.00	72.20	-	55.45	-	-
5	9.91	15.57	28.17	8.92	17.73	-	8.00
6	3.88	4.96	7.09	3.50	5.81	3.22	2.58
7	1.80	1.62	2.56	1.77	2.11	1.03	1.20
8	0.78	0.54	0.91	0.70	0.68	0.33	0.50
9	0.29	0.18	0.31	0.26	0.28	0.13	-
10	0.08	0.06	0.10	0.07	0.10	0.07	-
11+	-	-	-	-	-	0.06	-

$$P_i = P_i^* x_i \quad (7)$$

$$P = \sum_{P_i \in L} P_i \quad (8)$$

Where

P_i is partial pressure of pseudo-component i in mixture (psi),

P_i^* is pure component vapor pressure of pseudo-component I (psi),

x_i is molar fraction of pseudo-component i in mixture,

P is true vapor pressure of mixture (psi) and

L is pseudo-component group belonging to lumped composition model defined earlier (subchapter 9.2).

True vapor pressures of mixtures were converted to Reid vapor pressure with Equation 9 based on equation from US Environmental Protection Agency (EPA) (2006). The original equation has been derived by fitting equation to a monograph from American Petroleum Institute (API) and for this work the equation has been reversed from calculating true vapor pressure from Reid vapor pressure to calculating Reid vapor pressure from true vapor pressure.

$$RVP = 10^{\frac{ln(P)+\frac{7261}{T+459.2}-12.82}{\frac{2799}{T+459.6}-2.227}} \quad (9)$$

Where

RVP is Reid vapor pressure in psi,

P is true vapor pressure in psi and

T is temperature in °F.

9.6.3 Distillation Curve Model

Refinery blending pool model (introduced in subchapter 9.7) takes six distillation curve points of blending components as input. These points are known as E-values and they represent the volumetric percentage of blending component that has evaporated at a specific temperature. The refinery blending pool model uses these values for blending product property calculations. E-values considered in the model are E70, E95, E100, E105, E110, and E180, which represent the evaporated volume percentage in corresponding Celsius degree temperatures. Since the value of synthetic and FCC hydrocarbon mixtures considered in this work were estimated using the aforementioned blending pool model, these E-values needed to be calculated.

The distillation curve model used in this work is based on assumption that studied mixtures are rather ideal and boiling points of pure components represent with sufficient accuracy the evaporated volume in the mixtures. For simplicity, an absolute boiling point (instead of more realistic boiling temperature region) was determined for each pseudo-component. This was done by calculating an average of boiling points for compounds that are represented in each pseudo-component. Using single boiling point for a pseudo-component that represents multiple real components and assumption of ideality of mixture were recognized to be coarse generalization. However earlier experiments had shown that E-values were not key limiting properties in refinery blending model, so accurate estimates were not essential. The boiling points of pseudo-components are shown in Table 13.

Table 13. Boiling points (°C) of pseudo-components for the distillation curve model.

Carbon no.	Naphthenes	n-Paraffins	i-Paraffins	Cyclo-Olefins	Olefins	Aromatics	Methyl Ethers
3	-	-42.04	-	-	-	-	-
4	-	-0.50	-11.72	-	-2.14	-	-
5	49.25	36.06	18.67	44.23	27.78	-	55.20
6	76.26	68.73	59.39	72.25	64.77	80.09	86.30
7	96.15	98.20	87.09	98.90	92.23	110.63	102.00
8	120.67	125.68	114.89	129.19	115.95	139.53	115.00
9	145.24	150.82	137.81	156.00	145.59	163.80	-
10	175.73	174.15	160.77	179.00	169.50	183.67	-
11	-	-	-	-	-	200.00	-

Each E-value is calculated as sum of component volume fractions that have boiling point below the E-value's temperature. The formulas for E-value calculations are presented in equations 10–15.

$$E70 = \sum_{V_c \in L,\, T_c < 70\ ^\circ C} V_c \tag{10}$$

$$E95 = \sum_{V_c \in L,\, T_c < 95\ ^\circ C} V_c \tag{11}$$

$$E100 = \sum_{V_c \in L,\, T_c < 100\ ^\circ C} V_c \tag{12}$$

$$E105 = \sum_{V_c \in L,\, T_c < 105\ ^\circ C} V_c \quad (13)$$

$$E110 = \sum_{V_c \in L,\, T_c < 110\ ^\circ C} V_c \quad (14)$$

$$E180 = \sum_{V_c \in L,\, T_c < 180\ ^\circ C} V_c \quad (15)$$

Where

V_c is volume fraction of pseudo-component,

L is pseudo-component group belonging to lumped composition model defined earlier in subchapter 9.2,

T_c is boiling point of the pseudo-component (C°).

9.7 Refinery Blending Pool Model for Product Value Estimation

One approach to determine naphtha value is with a refinery blending pool model. Basic idea of this method is to add naphtha as blending component to it. When gasoline product and other blending component values are known, naphtha value can be estimated based on increase in refining margin after inclusion of naphtha into the blending pool. Blending pool model's basic principle has been illustrated in Figure 12.

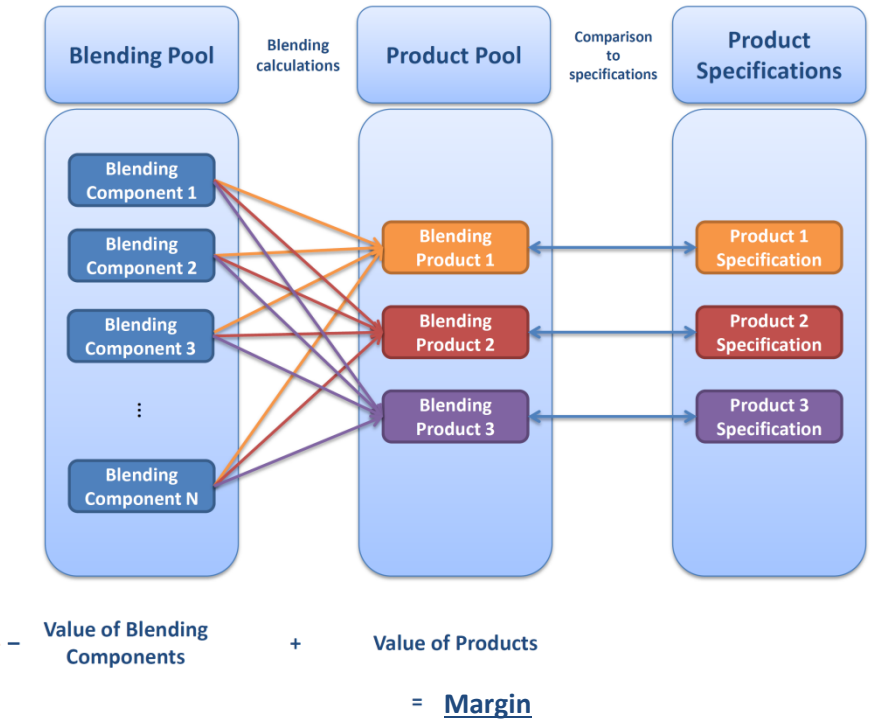


Figure 12. Basic concept of the blending pool model.

Calculation logic of the blending pool model used in this thesis was largely based on Halinen's (2002) model. Its features were reviewed and modified as needed. Blending pool model of this thesis (referred as *the model* here after) and modifications made to it compared to original version are briefly described in this subchapter. A more detailed description of the model can be found from Halinen's (2002) thesis. The model takes into account 15 blending component properties which are the following:

- RON
- MON
- Reid Vapor Pressure (RVP)
- Specific gravity
- E70, vol-%
- E95, vol-%
- E100, vol-%
- E105, vol-%

- E150, vol-%
- E180, vol-%
- Sulfur content (wt-ppm)
- Benzene vol-%
- Olefin, vol-%
- Aromatics, vol-%
- Oxygen, wt-%.

Properties of blending products need to be calculated in order to compare the product to gasoline specifications. Some gasoline properties blend linearly. These include specific gravity, E70–E180 values, sulfur content, benzene vol-%, olefin vol-%, aromatics vol-%, and oxygen vol-%. Blending product sulfur content is calculated as an average of blending component weight fractions (Equation 16) and other linearly blending properties as an average of blending component volume fractions (Equation 17):

$$P_{prod.} = \sum_i P_{comp.,i} w_{comp.,i} \quad (16)$$

$$P_{prod.} = \sum_i P_{comp,i} \varphi_{comp,i} \quad (17)$$

Where

$P_{prod.}$ is value of property in blending product,

$P_{comp.,i}$ is value of property in blending component i,

$w_{comp.,i}$ is weight fraction of blending component i, and

$\varphi_{comp.,i}$ is volume fraction of blending component i.

Octane numbers and Reid vapor pressure are properties that do not blend linearly (Baird 1989). Instead of linear blending equations, Chevron method (Baird 1989) was used for estimating RVP blending and Ethyl method (Baird 1989) was used for estimating octane number blending. Chevron method converts RVP values to blending index RVP (RVPI), blends RVPI values linearly by volume fraction, and converts RVPI values back to RVP values. The calculation formula is presented in Equation 18:

$$RVP_{prod.} = \left(\sum_i \left({RVP_{comp.,i}}^{1.25} \varphi_{comp.,i} \right) \right)^{0.8} \quad (18)$$

Where

$RPV_{prod.}$ is Reid vapor pressure of blending product (kPa),

$RPV_{comp.,i}$ is Reid vapor pressure of blending component I (kPa), and

$\varphi_{comp.,i}$ is volume fraction of blending component I (kPa).

Ethyl method or "RT-70" method (Gasoline Blending Plus 2008) is an old octane blending calculation method from 1950's (Baird 1989). The equations of these methods are quite lengthy and are also presented in many sources (Baird 1989, Maples 2000, Halinen 2002) so they were left out of this thesis. Noteworthy characteristic of Ethyl method is that it is not suitable for octane blending calculations of oxygenates (Gasoline Blending Plus 2008). Therefore special blending octane numbers were used for this purpose to model the nonlinear octane blending behavior.

Three different refinery blending pools were introduced in Halinen's (2002) thesis to imitate gasoline blending in a US Gulf Coast refinery, a European refinery, and a Californian refinery. The same three blending pools were also used in this thesis with minor fixes. After year 2002 gasoline specification sulfur limits have become stricter and high sulfur FCC naphtha has become less suitable as component for modern gasoline. Therefore octane numbers and sulfur contents of FCC component in European refinery were reduced to simulate the inclusion of desulfurization unit after FCC unit. The modified blending pools and their component properties are listed in APPENDIX 3. Also gasoline specifications were updated to correspond to currently valid specifications which are presented in Table 14.

Table 14. Gasoline specifications in the blending pool model.

Refinery	Gulf Coast refinery			European refinery			Californian refinery		
Specification	**US RFG premium**	**US RFG regular**	**US Conventional regular**	**Euro 5 98 E5**	**Euro 5 95 E5**	**Euro 5 95 E10**	**CaRFG Premium**	**CaRFG Midgrade**	**CaRFG Regular**
Sulfur (wt-ppm)	30	30	30	10	10	10	20	20	20
Benzene vol-%	0.6	0.6	1.1	1.0	1.0	1.0	0.7	0.7	0.7
Aromatics vol-%	19.8	19.8	26.1	35	35	35	22	22	22
Olefin vol-%	11.2	11.2	11.6	18	18	18	6	6	6
RVP (kPa)	59.3	59.3	68.3	60+[1]	60+[1]	60+[1]	54	54	54
Oxygen wt-% (max)	2.7	2.7	2.7	2.7	2.7	3.7	2.2	2.2	2.2
Oxygen wt-% (min)	2.0	2.0	0	0	0	0	1.8	1.8	1.8
RON	-	-	-	98	95	95	-	-	-
MON	-	-	-	88	85	85	-	-	-
AKI	92	87	92	-	-	-	92	89	87
E100	-	-	-	46	46	46	-	-	-
E150	-	-	-	75	75	75	-	-	-
T50	103	103	103	-	-	-	100.6	100.6	100.6
T90	166	166	166	-	-	-	151.7	151.7	151.7

[1]According to EN Standards (2012) Euro 5 RVP limit increases in function of gasoline's bioethanol content. The increase of RVP maximum, Euro 5 RVP limit was estimated with formula $RVP_{max} = 60 + (-0.00267029 \cdot V_{bioethanol}^4 + 0.0816540 \cdot V_{bioethanol}^3 - 0.922558 \cdot V_{bioethanol}^2 + 4.50601 \cdot V_{bioethanol})$ where $V_{bioethanol}$ is volumetric percentage of bioethanol in gasoline and RVP_{max} is maximum RVP of gasoline in kPa.

Optimization model maximizes refinery's margin, which is calculated as difference between value of gasoline product and value of spent blending components (see Equation 19):

$$MAX(\sum_{g=1}^{3} val_g V_g - \sum_{b=1}^{m} val_b V_b) \quad (19)$$

Where,

val_g is gasoline value ($),

val_b is value of blending component ($),

V_g is gasoline volume (bbl),

V_b is volume spent blending component (bbl),

g is gasoline grade (1 … 3), and

b is gasoline blending component (1 … m)

In this context gasoline and blending component value means their monetary value at refinery site. Assumption is that unspent components of the blending pool can be sold. Updated values of gasoline products and blending components were based on price data from McGraw Hill Financial (2014), Argus Media (2014), and EIA (2014). The prices represent market situation in March 2014. The prices that could not be found from data resources were estimated by comparing blending component properties. The Values of blending components that are produced in a petroleum refinery were slightly reduced from the prices that data sources suggested. This was done in order to take into account the additional costs that are related to assumed lack of steady markets of these products (compared to gasoline). The applied component prices and gasoline prices are listed in APPENDIX 4.

10 Compositions and Properties of Naphthas

This chapter details compositions, basic properties, and olefin distributions of studied naphthas. The compositions of researched naphthas are introduced using the composition model. Furthermore some basic properties of the naphthas are listed. Distillation of naphthas was modelled in order to gain basic understanding of how olefins (reacting components in hydrogenation and etherification) are distributed in the different fractions of the naphthas.

10.1 Introduction to Studied Naphthas

Four synthetic naphthas and two FCC naphthas were selected as the study subjects of this research. All naphtha compositions were acquired from Neste Jacobs' internal sources. Properties of naphthas were estimated with calculation models introduced in chapter 9 or (in case of sulfur content) approximated. Calculated and estimated basic properties of the naphthas are presented in Table 15. More precise compositions of the naphthas are presented in APPENDIX 6.

Table 15. Calculated and estimated basic properties of studied naphthas.

Naphtha	Synthetic Naphtha 1	Synthetic Naphtha 2	Synthetic Naphtha 3	Synthetic Naphtha 4	FCC Naphtha 1	FCC Naphtha 2
RON	91.90	90.68	90.94	89.39	94.95	84.84
MON	76.73	76.67	76.36	76.39	80.68	73.37
AKI	84.32	83.67	83.65	82.89	87.82	79.10
RVP (kPa)	44.42	53.49	43.86	55.79	145.49	46.22
Specific gravity	0.7410	0.7728	0.7409	0.7148	0.6395	0.7265
Average molar weight (g/mol)	92.38	89.08	91.94	87.99	67.97	94.688
Sulfur (wt-ppm)	0.00	0.00	0.00	0.00	10	10
Benzene (vol-%)	0.08	0.07	0.09	0.06	1.11	0.46
Olefins (vol-%)	22.57	31.19	35.09	27.08	53.35	51.57
Aromatics (vol-%)	26.54	18.26	27.63	13.85	2.59	18.32

Octane numbers of all naphthas are in the typical range of gasoline blending components (see APPENDIX 3 for comparison). Highest octane number values are found from FCC naphtha 1 and lowest from FCC naphtha 2. Gasoline grade naphtha's low molecular weight components have typically higher octane number than the heavy components of the same molecular group (see Table 9 and Table 10), so in that sense octane numbers and molecular weights of the naphthas seem to be logical and therefore plausible. Measured data of synthetic naphtha sulfur contents were not available, but due to general non-sulfuric nature of synthetic naphtha, the sulfur contents were assumed to be zero. Measured data of FCC naphtha sulfur content was not available either. It is, however, known that both FCC naphthas were desulfurized. This indicates that FCC naphtha sulfur contents are likely to be around 5-20 wt-ppm. For calculations, the value of 10 wt-ppm sulfur was used in this thesis for both FCC naphthas. Benzene contents of synthetic naphthas are negligible, but significant in FCC naphthas (benzene limits in modern gasoline specifications are around 0.6–1.1 vol-%, see Table 14). Olefin contents in all naphthas are significant compared to olefin limits in gasoline specifications, which is essential for this study. Value maximization is studied with processing units that reduce olefins and this is meaningful only with olefin-rich naphthas. Synthetic naphtha olefin vol-% is approximately 30, whereas FCC naphtha olefin contents are over 50 vol-%. Aromatics content is roughly around 20 vol-% in all

naphthas except FCC naphtha 1, which has low aromatics content. This is sensible, since FCC naphtha 1 is remarkably lighter than the other naphthas. Aromatic components carbon number start from C6 by nature and have higher boiling points than other naphtha molecules of the same carbon number (see Table 13). Therefore aromatics tend to enrich into heavier naphtha fractions rather than the light ones.

10.2 Analysis of Olefin Content in Naphtha Fractions

Olefins are reacting components in selective hydrogenation and etherification. In order to understand which naphtha fractions would be the most suitable for etherification and hydrogenation, olefin contents of naphtha fractions were studied. Since olefin limits in gasoline specifications are expressed in volume percentages of olefins, the olefin content of naphtha fractions are also presented in volume basis. The olefin contents in naphtha fractions are shown in Figure 13.

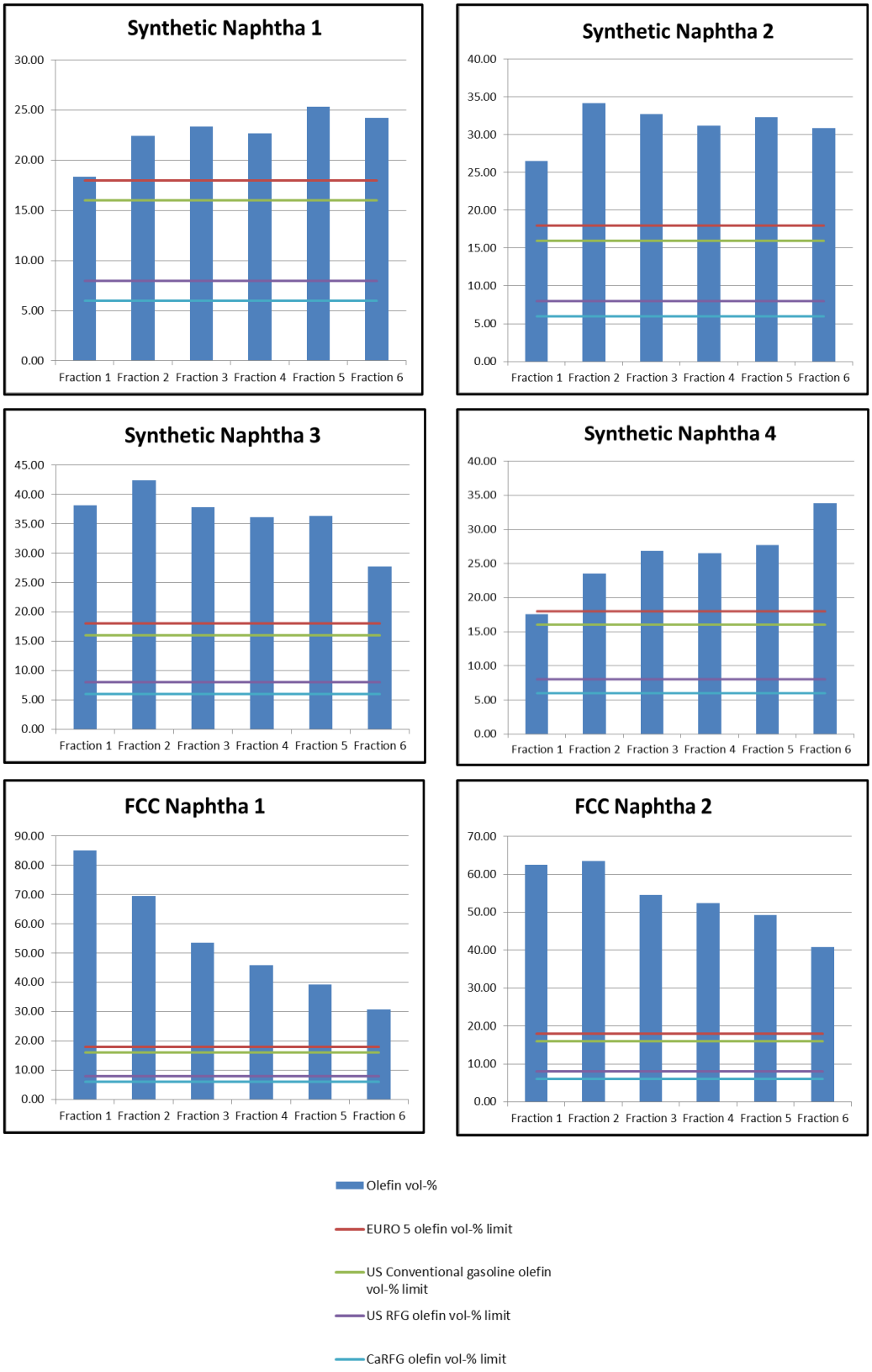


Figure 13. Olefin content (volume percentage) of naphtha fractions in synthetic naphthas 1–4, FCC naphthas 1–2 and olefin limits in some gasoline specifications.

According to the results presented in Figure 13 all studied naphthas have significant olefin content in all six naphtha fractions. In other words, olefins are not concentrated only in heavy or light ends of naphthas. All naphthas have olefin content above almost any of the examined gasoline standards. The only exception to this is the lightest fraction (fraction 1) of synthetic naphtha 4, which has slightly lower olefin content than the olefin limit of Euro 5 gasoline. Synthetic naphthas 1–3 seem to have somewhat flat volumetric distribution of olefins in all fractions. Synthetic naphtha 4 has more olefins in heavy fractions whereas both FCC naphthas have more olefins in light fractions. As a conclusion, all the studied naphthas are olefin-rich blending components if used in gasoline blending pool without treatment. Olefins are also present in all fractions, so any fraction of the naphthas could not yet be ruled out as a possible feed for hydrogenation or etherification.

11 Effect of Processing on Product Properties

In order to suggest any processing alternatives for naphthas, the effect of hydrogenation and etherification on naphtha properties had to be examined by simulations with kinetic model of hydrogenation and conversion model of etherification (introduced in chapter 9). Some interesting treatment options were considered. These included processing of only certain naphtha fractions and combination of two processing units. To understand what processing scenarios might produce highest profit, hydrogenation and etherification of each naphtha fraction was individually simulated.

11.1 Effects of Naphtha Fraction Hydrogenations

One of the subjects of this study is to examine which fractions of the naphthas are optimal for hydrogenation feed. This question was approached by studying what kind of effect hydrogenation does have on the naphtha properties. Properties considered here are MON, RON, AKI (average of RON and MON), Reid vapor pressure, olefin volume percentage, and specific gravity. These were selected since the properties are affected by hydrogenation, they are restricted in gasoline specifications, and/or they were expected to have strong effect on naphtha value. The effect of hydrogenation on naphtha properties for synthetic naphthas 1–4 and FCC naphthas 1–2 are shown in figures and tables of APPENDIX 7, which illustrate naphtha properties in cases with no hydrogenation, hydrogenation of single fractions, and hydrogenation of all fractions

simultaneously. The fractions were hydrogenated to point where olefin content of hydrogenation product equals 2.5 wt-%. The reason for this was the suspicion that further saturation might cause aromatics to start saturating in a real process and hydrogenation would no longer be selective.

The results of hydrogenation were somewhat similar with all naphthas. Some general notions were made from all six naphthas:

- Hydrogenation of heaviest three fractions (4, 5, and 6) had more positive effect on octane numbers than hydrogenation of lightest three fractions (1, 2, and 3). Hydrogenation of three heaviest fractions mostly rose or maintained RON, MON and AKI values while hydrogenation of lightest three fractions tended to lower the octane numbers.
- Hydrogenation of heaviest three fractions did not have significant effect on RVP while hydrogenation of lightest three fractions slightly increased the value of RVP.
- Reduction of olefin volume percentage was expectedly directly proportional to the initial content of olefins in hydrogenated fraction.
- Reduction of specific gravity was typically more pronounced in hydrogenation of three lightest fractions than the heaviest three. However the changes in specific gravity were in each case negligible.

These results indicate that hydrogenation of three heaviest fractions of synthetic naphthas is more beneficial than hydrogenation of lightest three fractions. Higher octane numbers and lower RVP were considered to be major benefits compared to slightly lower specific gravity gained with hydrogenation of lightest three fractions. Yet the significance of each property depends ultimately on large number of variables, such as key restricting properties of refinery's gasoline blending pool.

11.2 Effect of Naphtha Fraction Etherifications

Similarly to the effect of hydrogenation, the effects of etherification were studied for synthetic naphthas 1–4 and FCC naphtha 1–2. Once again, the effect of each fraction's treatment was studied individually to find out which fractions of the naphthas are the

most beneficial to process. The detailed results (tables and figures) of this study are presented in APPENDIX 8.

Common discoveries made from the naphtha etherification results were the following:

- Most significant effect on properties was gained by etherification of light fractions (especially fraction 1 and 2). This was expected since light olefins of the mixtures have the highest conversion rates in etherification.
- Oxygen wt-% in naphthas increased slightly. However oxygen content stayed below 3.6 wt-% in all synthetic naphthas even with all fractions etherificated.
- Etherification increased all octane numbers and decreased vapor pressure.
- Minor increases in specific gravity were caused by etherification.

As a conclusion, etherification has positive effect in octane number and vapor pressure, but on the negative side it rises oxygen content and slightly increases specific gravity. Most of reactive olefins are in the light fractions so etherification of those fractions seem be the most meaningful choice. As in case of hydrogenation, positive effects of etherification seem to overcome the negative ones. However, whether the positive effect on some naphtha properties increases the naphtha value enough to justify the investment to the process could not yet be concluded.

12 Processing Cost Calculations

While processing of naphtha may increase naphtha value, the profitability of processing depends largely on costs of processing. Hence operating costs of hydrogenation and etherification were estimated.

Three operating costs were initially considered for hydrogenation: cost of hydrogen, pumping from 1 bar to 30 bar pressure, and feed heating costs. Cost of catalyst in hydrogenation was estimated to be mostly initial investment cost, so it is covered later in investment costs section. Hydrogenation units are typically equipped with one or more preheating steps before and/or between hydrogenation reactors to obtain the desired reactor temperature (Bloch 2006) and they require heating utilities. However, hydrogenation reactions are strongly exothermic (Leorince 2001). Therefore it was assumed that the heat required for preheating of the feed flow can be drawn from the

hydrogenation product flow. Also the feed is already in reasonably high temperature after previous fractionation step so required heating duty is not likely very high. With these observations in mind operating costs of heating were considered negligible. Therefore pumping costs and hydrogen costs were left as the main operating costs in hydrogenation.

Pumping cost of hydrogenation was estimated by simulating pumping of a model mixture from 1 bar pressure to 30 bar pressure (the selected pressure in hydrogenation unit). Simulation was performed with Aspen plus pump module using default pump properties. The results indicated pumping cost of $ 2.17 per ton in gulf coast area (with assumed electricity price $ 0.10 per kWh (EIA 2014)), which corresponds to cost of $ 1 170 per day when studied daily naphtha production (540 t/d) is fed into hydrogenation. This estimate is likely to be too low in Europe, but since cost of pumping is almost negligible compared to hydrogen cost, this error was not considered significant.

Hydrogen cost was estimated based on report from U.S. Department of Energy (2012). This report estimates hydrogen expense to be 4 490 $ per metric ton for hydrogen produced with steam methane reforming from natural gas. Very similar estimate (5 000 $ per metric ton) was found from calculations of Blencoe (2009). Since steam methane reforming consumes natural gas as main resource of hydrogen, hydrogen cost must partly depend on natural gas. Actual portion of natural gas price in hydrogen production expenses could not be defined, so the same hydrogen cost was used in all geographical areas (North America and Europe). This was regardless of the fact that the hydrogen price was based on relatively low natural gas prices in the United States. Selected hydrogen price (4 490 $ per metric ton) corresponded to daily hydrogen expenses of $ 11 636 – 45 279 with full hydrogenation of daily production (540 t/d) depending on examined naphtha.

Methanol was assumed to be a major operating cost of etherification. In this work methanol is considered as operating cost since it is compulsory raw material in order to process naphtha into methyl ethers. Based on price reported by Methanex (2014), methanol cost was estimated to be 590 $ per metric ton. This corresponds to methanol cost of $ 1 341 – 7 569 per day with full naphtha etherification (feed 540 t/d) depending on examined naphtha. In addition to methanol, steam was estimated to be a significant cost. Steam expenses were calculated based on steam price of $ 40 per metric ton and

consumption of 0.8 metric tons steam per a metric ton of feed. Electricity consumption for a 540 t/d unit was estimated as 1500 kWh per day and for 270 t/d unit half of this. With assumed electricity price of 0.1 $ per kWh, this did not seem to be a major expense, but it was considered in operating cost calculations anyway.

In addition to actual operating costs, maintenance expenses were considered in daily costs. Maintenance was estimated to cost 2 percent of initial investment costs per year for both unit alternatives. The expenses of investment are discussed in chapter 13. In the following chapters operating costs are taken into account in profitability calculations. These include actual daily operating costs and cost of maintenance (2 percent of initial investment costs of unit per year).

13 Investment Cost Analysis for Example Unit Configurations

A very important factor in profitability of a process is its initial investment cost. The subject of this chapter is estimation of the investment costs for both hydrogenation and etherification units. For simplicity, the investment cost estimation was done with single naphtha only (synthetic naphtha 2) and the results for other naphthas were assumed to be similar. Two daily feed capacities (540 t/d and 270 t/d) were taken into account.

13.1 Estimation of Hydrogenation Unit Investment Costs

Investment cost of hydrogenation unit was based on the following procedure:

1. Estimating required capital expenditure for major equipment (compressor, reactor, heat exchangers, pumps etc.)
2. Estimating unit investment cost with rule of thumb assumption that major equipment cost cover approximately 20 percent of total investment cost (which includes design, piping, infrastructure etc.) and adding the cost of catalyst.

Flow scheme for hydrogenation unit was selected to resemble Neste Jacobs's NExSat hydrogenation process (Neste Jacobs, 2014). Major differences compared to NExSat process are that catalyst is selective to olefin hydrogenation instead of aromatics hydrogenation and hydrogenation feed heating with product heat in NExSat was replaced with simple hydrogenation product cooling with water. The latter design decision was justified with minimal heating demand of already hot fresh feed.

Hydrogenation product recirculation rate was selected based selected maximum temperature rise in reactor (50 °C). Flow diagram of hydrogenation process is presented in Figure 14 and some key assumptions of process properties are listed in Table 16.

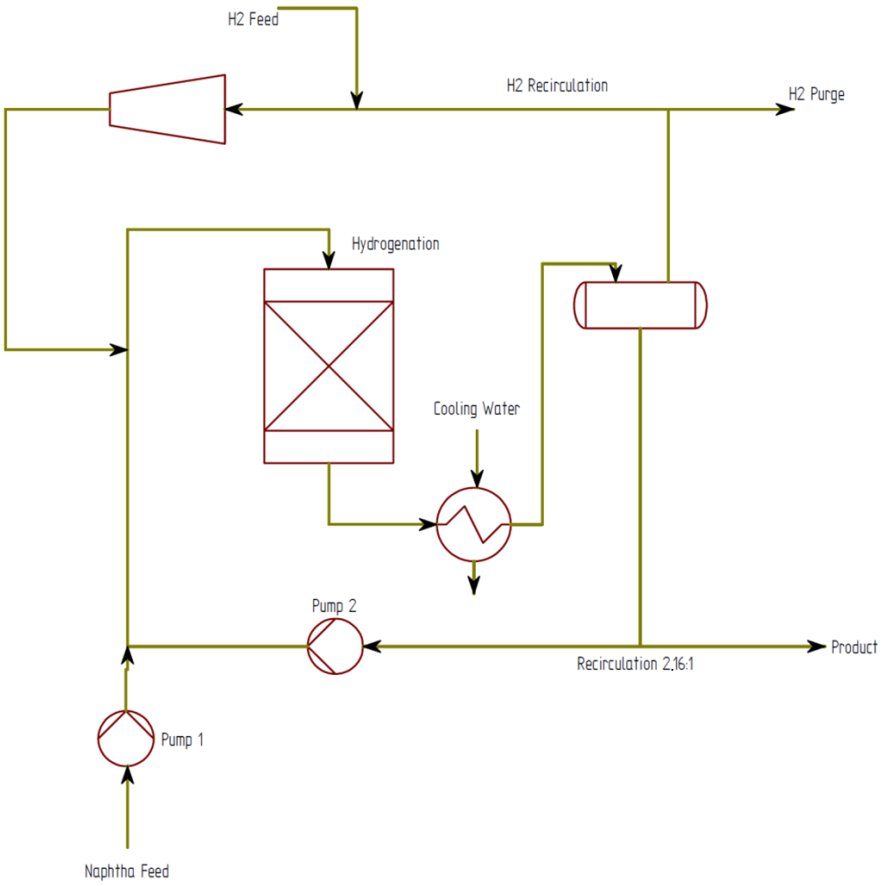


Figure 14. Flow chart of hydrogenation unit.

Table 16. Key design parameters of hydrogenation unit.

Property	Value	Description/reference
Average reactor temperature	160 °C	
Maximum allowed temperature rise in reactor	50 °C	Estimated safe temperature rise in hydrogenation reactor
Reactor pressure	30 bar	
Reaction enthalpy of olefin hydrogenation	-126 775 J/mol	(Utah Valley University 2009)
Hydrogen loss to purge flow	10 wt-% of H_2 feed	
Pressure drop through one loop	5 bar	estimated

After the basic concept of hydrogenation unit was fixed, the flow rates were calculated and the equipment sizes were estimated. Compressor and pump sizing was based on estimated flow rates and required pressure increases. Broad estimation of heat exchanger was based on required heating duty and required heat transfer area. The reactor size was estimated based on assumed WHSV of 1.0 h^{-1}. Finally the cost estimates were based on equipment cost data from McGraw Hill Higher Education (2003) plant cost database, after considering increase in plant expenses since 2002 and Neste Jacobs's internal sources. Categorized investment cost estimates are presented in Table 17. Accuracy of the total investment cost was estimated as +/- 50 %.

Table 17. Estimated investment costs of hydrogenation unit.

INVESTMENT COST ESTIMATES	Feed	Compressor	Reactor	Other Equpment	Catalyst	Total investment cost
Full hydrogenation	540 t/d	$ 640 000	$ 600 000 (22 m^3)	$ 600 000	$ 300 000	$ 9 500 000
Partial hydrogenation	270 t/d	$ 460 000	400 000 (11 m^3)	$ 400 000	$ 200 000	$ 6 500 000

13.2 Estimation of Etherification Unit Investment Costs

Investment cost of etherification unit was evaluated with a similar procedure as hydrogenation unit:

1. Estimating required capital expenditure for major equipment (reactor, distillation columns, pumps, heat exchangers etc.)
2. Estimating unit investment cost with assumption that major equipment cost cover approximately 20 percent of total investment cost.

Etherification technology NExEthers from Neste Jacobs was selected as the basis of etherification unit (Neste Jacobs, 2014).

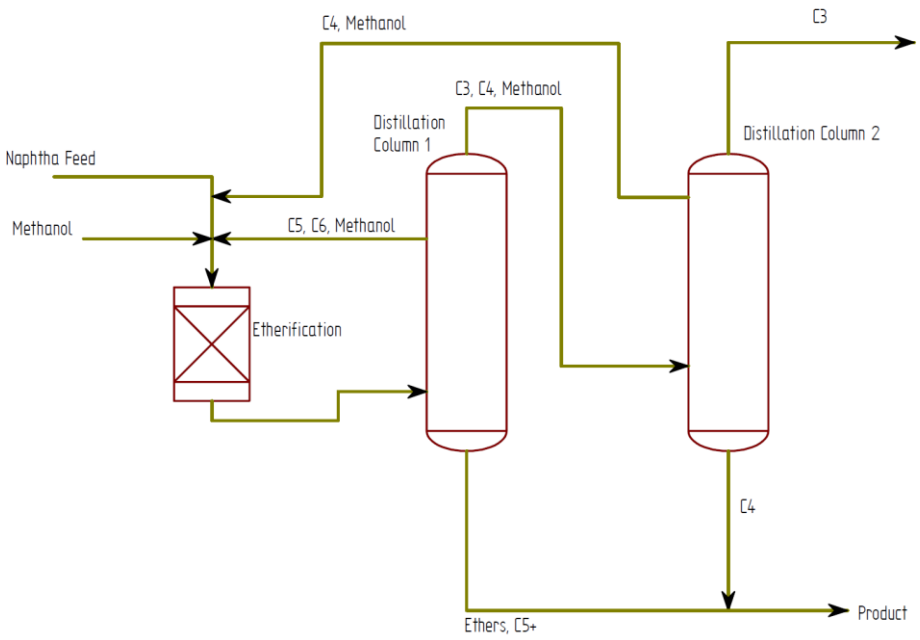


Figure 15. Flow diagram of etherification unit.

Approximate flow rates in system were calculated, which revealed, that since the amount of C4- hydrocarbons in synthetic naphtha 2 is negligible, second separation could be performed with small and simple column. Purpose of this column is mainly to recycle methanol and stop C3 and C4 hydrocarbons from getting enriched into system. First separation is difficult since C5 olefins should be partly separated from other C5 hydrocarbons. For cost estimating purposes the first column was estimated to have 50 stages and second one 10 stages. The reactor was assumed to operate at WHSV 0.5 h^{-1}. It is also notable that investment costs for methanol logistics of etherification would probably be low in a methanol-to-naphtha plant, since these facilities consume methanol even without an etherification unit. Estimates of equipment costs and total

investment costs are presented in Table 18. Accuracy of the total investment cost was estimated as +/- 50 %.

Table 18. Estimated investment costs of etherification unit.

INVESTMENT COST ESTIMATES	**Feed**	**Reactor**	**Column 1**	**Column 2**	**Other equpment (pumps etc.)**	**Total investment cost**
Full Etherification	540 t/d	$ 1 200 000 (70 m^3)	$ 1 000 000	$ 600 000	$ 2 200 000	$ 25 000 000
Partial Etherification	270 t/d	800 000 (35 m^3)	$ 600 000	$ 400 000	$ 1 600 000	$ 17 000 000

13.3 Comparison of Investment Costs

According to above estimates, etherification unit investment cost is around 2.5 times the cost of hydrogenation unit. Highest investment expenses are expected for combination of hydrogenation and etherification and for full etherification (for definitions of processing scenarios, see Subchapter 14.1). For comparison estimated total investment costs have been illustrated in Figure 16, which shows the expenses in scenarios of processing half or all of example feed (540 t/d) in etherification unit and/or hydrogenation unit.

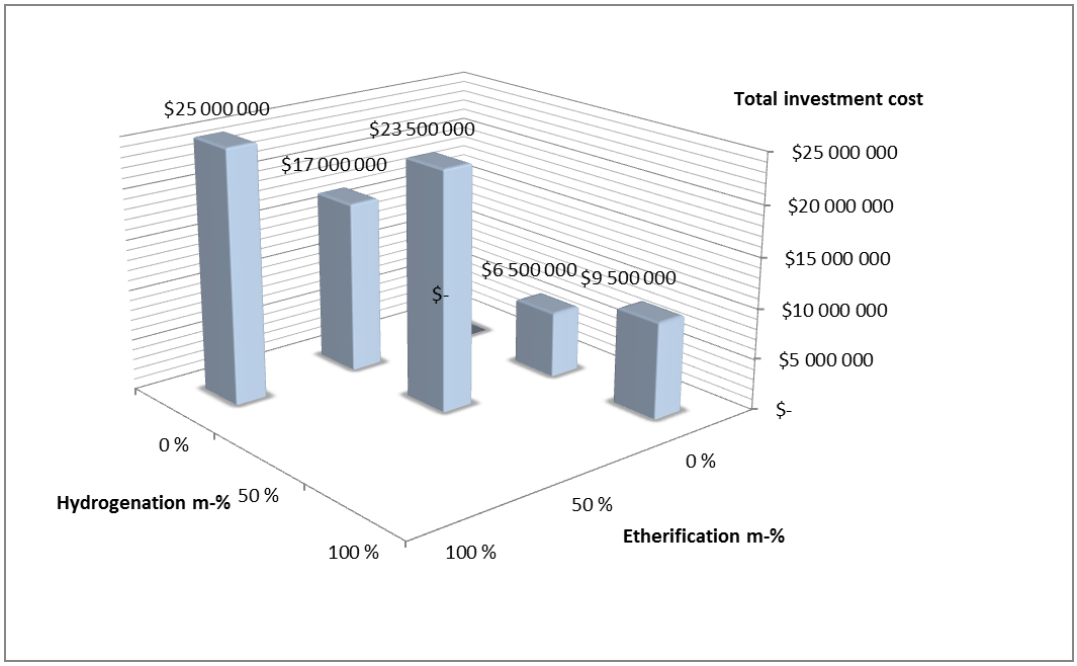


Figure 16. Comparison of processing scenario estimated investment costs.

14 Effect of Hydrogenation and Etherification on Product Value and Analysis of the Process Feasibilities

This chapter focuses on the feasibility of naphtha processing alternatives. The studied processing scenarios were defined and three different approaches were taken to analyze the feasibility of each scenario. Firstly the feasibilities of the scenarios were analyzed by comparing processed and unprocessed naphtha products to Colonial Pipeline specifications. Secondly the product suitability for catalytic reforming feed was considered. Finally the naphtha values were analyzed with refinery blending pool models.

14.1 Studied Processing Scenarios

Based on findings on the effect of hydrogenation and etherification on naphtha properties (chapter 11), six processing scenarios were chosen for further investigation. These scenarios are presented in Table 19. These six scenarios were selected for a number of reasons:

- selection of etherification as primary processing alternative for light end and hydrogenation as primary processing alternative for heavy end was based on detected beneficial effects on naphtha properties in chapter 11
- selected set of scenarios enable general level comparison of hydrogenation and etherification profitability
- investigating half and full hydrogenation and etherification of naphthas gives approximate estimate of dependency between the level of processing and profitability of the processing
- scenario with combined hydrogenation and etherification indicates whether or not the combination of two processing methods is superior compared to single unit alternative.

Table 19. Hydrogenation and etherification scenarios chosen for further investigation.

Processing Scenario Number	**Scenario Description**	**Hydrogenated Fractions**	**Etherificated Fractions**	**Untreated fractions**
1	No treatment	-	-	1–6
2	Heavy fractions into hydrogenation	4–6	-	1–3
3	All fractions into hydrogenation	1–6	-	-
4	Light fractions into etherification	-	1–3	4–6
5	All fractions into etherification	-	1–6	-
6	Heavy fractions into hydrogenation, light fractions into etherification	4–6	1–3	-

Effects of processing scenarios on properties of naphthas were calculated and results are presented in APPENDIX 9. The results were analyzed and the following observations were made:

- Highest **RON value** was reached by full and partial etherification and combined hydrogenation and etherification (processing scenarios 4, 5, and 6).

- Highest **MON value** was achieved with synthetic naphthas by full hydrogenation and combined hydrogenation and etherification (processing scenarios (PS) 3 and 6) and with FCC naphthas by combined hydrogenation and etherification (PS 6). As exception from other naphthas FCC naphtha 2 suffered from collapse of MON value with full hydrogenation (PS 3). The reason seemed to be that FCC naphtha 2 contained high amount of C6–C10 non-cyclic olefins that saturate to n-paraffins and i-paraffins with low MON values.
- Highest **AKI value** was realized, without exceptions, with combined hydrogenation and etherification (PS 6).
- Lowest **RVP value** almost equally achieved with partial etherification, full etherification, and combined etherification and hydrogenation (PS 4, 5, and 6).
- Lowest **olefin volume fraction** was attained with full hydrogenation and combined hydrogenation and etherification (PS 3 and 6). With FCC naphtha 1 equally low olefin content was achieved with full etherification (PS 5). This was likely because FCC naphtha 1 contained high fraction of light olefins that are very reactive in etherification.
- Lowest **specific gravity** was achieved with full hydrogenation, partial hydrogenation, and no-treatment (PS 3, 2, and 1) in that order.
- Zero **oxygen weight-fraction** was expectedly reached with hydrogenation and no-treatment scenarios (PS 1, 2, and 3). Highest oxygen content was got with full etherification (PS 5) and slightly lower content with partial etherification and combined hydrogenation and etherification.

14.2 Comparison of Naphthas and Colonial Pipeline Product Specifications

Colonial Pipeline is the most significant fuel transportation pipeline in North America and so the naphtha product compatibility with Colonial Pipeline specifications may have significant impact on naphtha production profitability on East Coast and Gulf Coast areas in the US. This subchapter discusses the comparisons that were performed with synthetic naphthas 1–4 and FCC naphthas 1–2 with Colonial Pipeline's gasoline blendstock product specifications.

As presented in chapter 1, Colonial Pipeline has very widely defined Grade L specification, and number of grades (A, D, F, H, S, and T) that have well known market prices. If naphtha is distributed as Grade L, separate contract between buyer and seller is likely needed. Thereby possibility to transport naphtha as part of some of A, D, F, H, S, and T Grades (hereafter BOB-grades) can be a significant advantage, since it enables steady distribution channel for the product.

Oxygenates are prohibited in BOB-grades (Colonial Pipeline Company 2013). Hence processing scenarios with etherification were incompatible with the related specifications. However Grade L does not ban oxygenates, so all etherified products (processing scenarios 4–6) were found compatible with Grade L specification.

Oxygenates in etherified products made comparison to BOB-grades simple (not compatible), but far more interesting evaluation was possible with hydrogenated products. A study was performed in order to examine which specifications would be suitable for naphthas and how hydrogenation would influence on the results. The aim was also to find out which was the highest value specification that each naphtha could fulfill and how this would change, if naphthas were hydrogenated. The results are presented in Table 20. Vapor pressure limits were selected to match the RVP limit of blendstocks delivered in March (limits change every few months following the annual cycle of seasons) consistently with blendstock price data, which was also from March. It is also worthwhile to mention that BOB-grade specification property limits are to be met after blending the blendstock with 10 vol-% of ethanol. Therefore naphtha properties after blending with ethanol were calculated and comparisons with the BOB-grade specifications were performed with the properties after ethanol-blending of naphthas.

Table 20. Synthetic naphthas 1–4 and FCC naphthas 1–2 after processing scenarios 1–3 (see Table Table 19 for definitions) compared to Colonial Pipeline specifications. Table tells whether the naphtha fulfills requirements of a specification.

Naphtha	Specification: Specification description: Market Price* ($/bbl)	Grade A CBOB - 87 Octane 111.95	Grade D CBOB - 93 Octane 121.63	Grade F RBOB - 87 Octane 118.25	Grade H RBOB - 93 Octane 125.81	Grade S Atlanta CBOB - 87 Octane 109.96	Grade T Atlanta CBOB - 93 Octane 119.72	Grade L Gasoline Blendstocks -
Synthetic Naphtha 1:								
1 - No Treatment		yes	no	yes	no	yes	no	yes
2 - Half Hydrogenation		yes	no	yes	no	yes	no	yes
3 - Full Hydrogenation		yes	no	yes	no	yes	no	yes
Synthetic Naphtha 2:								
1 - No Treatment		yes	no	no	no	yes	no	yes
2 - Half Hydrogenation		yes	no	no	no	yes	no	yes
3 - Full Hydrogenation		no	no	no	no	yes	no	yes
Synthetic Naphtha 3:								
1 - No Treatment		yes	no	no	no	yes	no	yes
2 - Half Hydrogenation		yes	no	yes	no	yes	no	yes
3 - Full Hydrogenation		yes	no	yes	no	yes	no	yes
Synthetic Naphtha 4:								
1 - No Treatment		yes	no	no	no	yes	no	yes
2 - Half Hydrogenation		yes	no	no	no	yes	no	yes
3 - Full Hydrogenation		no	no	no	no	yes	no	yes
FCC Naphtha 1:								
1 - No Treatment		no	no	no	no	no	no	yes
2 - Half Hydrogenation		no	no	no	no	no	no	yes
3 - Full Hydrogenation		no	no	no	no	no	no	yes
FCC Naphtha 2:								
1 - No Treatment		no	no	no	no	no	no	yes
2 - Half Hydrogenation		no	no	no	no	no	no	yes
3 - Full Hydrogenation		no	no	no	no	no	no	yes

*Market prices presented are according to Argus Media (2014) March 2014 price data.

The results in Table 20 show that all studied naphthas fulfill the Grade L specification and all synthetic naphthas fulfill at least one of the BOB-grade specifications with all processing scenarios 1–3. However, neither of the FCC naphthas fulfilled BOB-grade specifications with any of processing scenarios 1–3. Vapor pressure of FCC naphtha 1 was too high in all cases, while octane numbers of FCC naphtha 2 were too low. The effects of hydrogenation on the highest value specification that naphtha fulfills were also studied and results are shown in Figure 17. Since FCC naphthas did not fulfill any BOB-grade specifications, they were left out of this study.

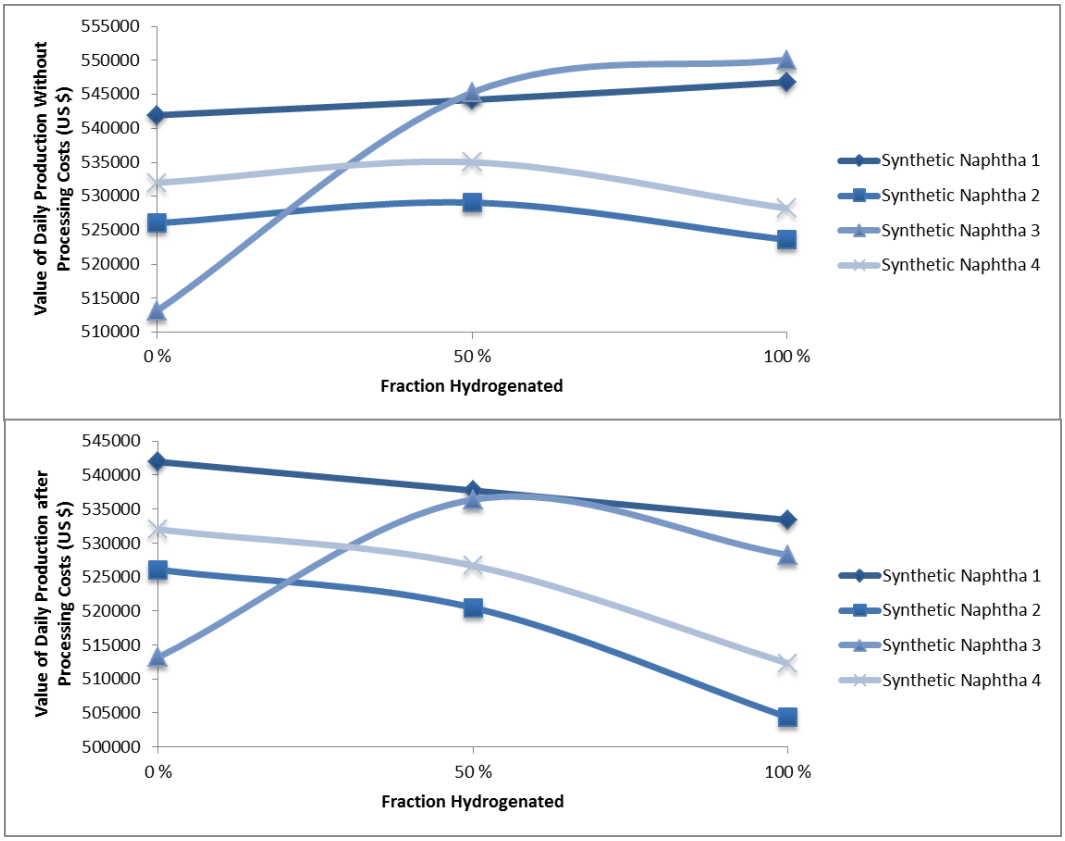


Figure 17. Effect of hydrogenation on the value of naphtha as Colonial Pipeline blendstock grade.

It was evident that the value of synthetic naphtha daily production depends on the most valuable specification that it can fulfill, and specific gravity. Without operating costs partial hydrogenation of synthetic naphthas seem to rise product value in all cases. Values per daily production capacity of synthetic naphthas 1, 2, and 4 were increased because their specific gravities decreased. Synthetic naphtha 3 also reached more valuable BOB-grade. Full hydrogenation boosted value of synthetic naphthas 1 and 3, but decreased value of synthetic naphthas 2 and 4 compared to partial hydrogenation. Values of nahpthas 1 and 3 increased because specific gravity of naphthas further decreased, but value of synthetic naphthas 2 and 4 dropped because RVP of naphthas exceeded Grade A limit. When operating costs were considered, only the value increase in partial hydrogenation of synthetic naphtha 3 seemed to surpass the operating costs.

Value analysis illustrated in Figure 17 can be criticized for being far too simple. The positive effect of processing on product properties leads to significant product value increase only if all requirements of a more valuable product grade become fulfilled. In

reality naphtha producer could blend gasoline components available on markets to naphtha so that it just barely fulfills the requirements of target grade. In order to take this into account, another case study was carried out.

Three blending components with good availability were selected to be blended with naphthas: n-butane, reformate, and toluene. N-butane is a mild octane booster with very high vapor pressure, toluene is very strong octane booster with low vapor pressure, and reformate has octane number and vapor pressure values somewhere between the two former components. For the sake of simplicity only single grade, 93 octane RBOB aka Grade H, was selected as the target product. Blending of naphthas with the three components was simulated and the amount of blending components was optimized to maximize profit. The definition of profit in this context is presented in Equation 20, and component costs and product values according to McGraw Hill Financial (2014) and Argus Media (2014) March 2014 prices are included in Table 21. The blending component costs were increased by two dollars per barrel from market data to include costs of transportation and handling.

$$P = val_{prod} \cdot V_{prod} - \sum_{b=1}^{m} cost_b V_b \quad (20)$$

Where,

P	is profit ($)
val_{prod}	is value of product per volume unit (RBOB 93 aka Grade H) ($/bbl),
val_b	is cost of blending component per volume unit ($/bbl),
V_{prod}	is volume of product (bbl),
V_b	is volume spent blending component (bbl),
b	is blending component (1 … m)

Table 21. Value of product and cost of blending components based on McGraw Hill Financial (2014) and Argus Media (2014) March 2014 price data.

Product/Component	Value/Cost (US dollars) per barrel
Product:	
• RBOB 93 (Grade H)	125.81
Blending Components:	
• n-butane	53.66
• reformate	141.44
• toluene	167.00

Results of Grade H production optimization are presented in Figure 18. FCC naphtha 1 was left out of this study since Grade H could not be produced from it with any realistic quantity of blending components due to its high vapor pressure. All studied naphthas showed increase in value when partially hydrogenated. After processing costs were taken into account only synthetic naphtha 3 and FCC naphtha 2 showed increase in value compared to cases without hydrogenation. Full hydrogenation seemed to mildly increase value of synthetic naphtha 1. Values of other naphthas decreased. When operation costs were taken into account, full hydrogenation did not seem economical with any naphtha.

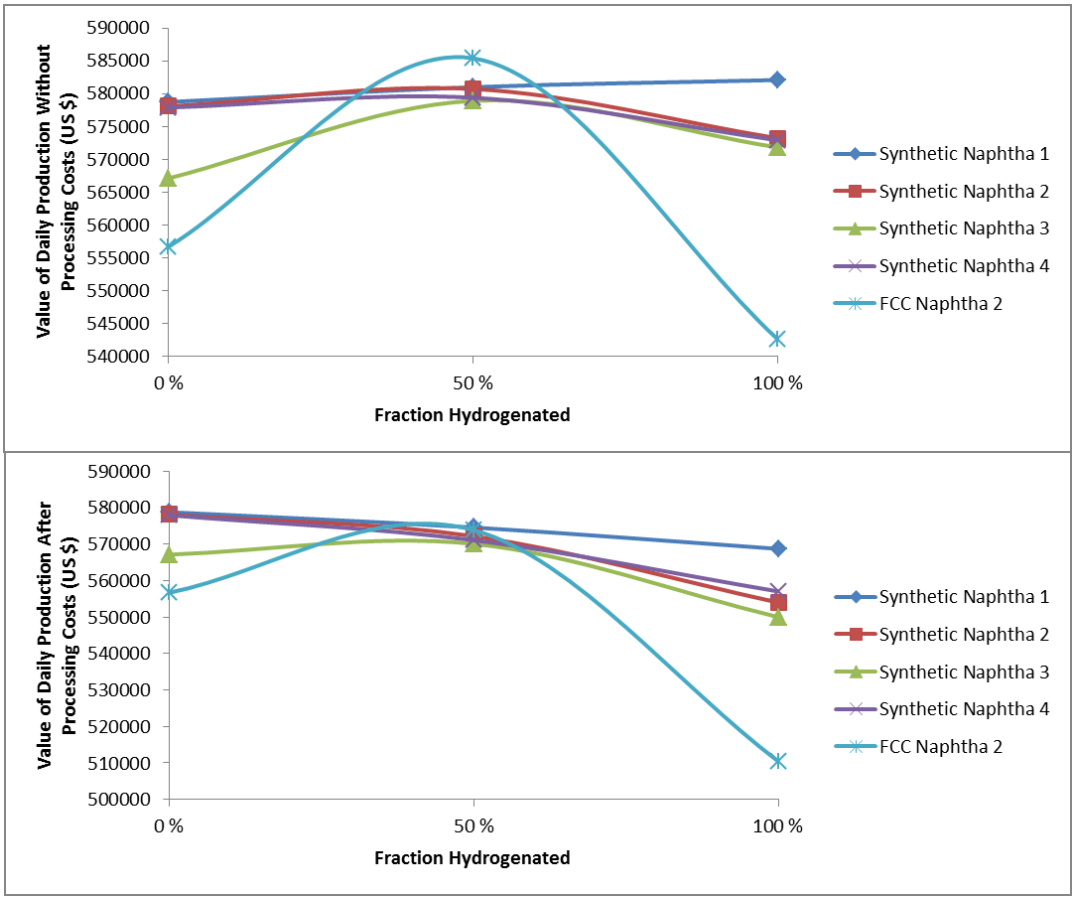


Figure 18. Blending profit of naphthas with and without processing costs in Colonial Pipeline Grade H production.

14.3 Suitability of Hydrogenation Products to Catalytic Reforming Feed

Option to process the selected naphthas with catalytic reforming was studied in this thesis because it might enable further increase in naphtha value. This examination was focused on evaluating whether the naphthas fulfill the technical and economical requirements for suitable catalytic reforming feed. No studies of catalytic reforming's effects on naphtha properties was performed.

As mentioned in chapter 1, catalytic reforming feed should not contain sulfur, nitrogen, halogens, oxygen, water, olefins, diolefins, arsenic or other metals. There was no reason to believe that the synthetic naphthas contained sulfur, nitrogen, halogens, or significant amounts of oxygen, water or metals. The same presumption was justifiable to the FCC naphthas with the exception that desulfurized FCC naphthas typically contain some

parts per million sulfur. However all the studied naphthas are rich in olefins and diolefins, so feeding them to catalytic reforming untreated was not an option. Considering possible treatment scenarios, feeding etherification product into catalytic reforming did not come into question since etherification product contains oxygen. This left hydrogenation product as the only considerable naphtha to feed in catalytic reforming. On this basis the only possible processing flow diagram would be similar to one presented in Figure 19.

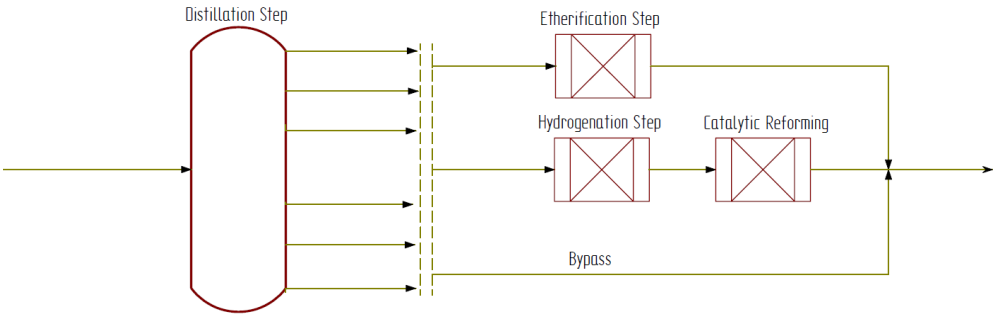


Figure 19. Flow diagram of process configuration containing catalytic reforming unit.

Suitability of each of the six naphtha fractions to catalytic reforming after hydrogenation step was analyzed. Some adventages and disadventages of each fraction are listed in Table 22. FCC naphtha 1 was found completely unsuitable for catalytic reforming because it had too low carbon number. As a result formation of aromatics would remain very low with this naphtha. Other Naphthas showed quite uniform results. Lighter fractions (1–3) had low content of C7+ hydrocarbons and contained C6 hydrocarbons, which made them a poor feed for catalytic reforming. Heavier fractions (4-6) typically had high content of C7-C10 hydrocarbons. On negative side n-paraffins were low in fractions 4–6. Formation of aromatics would have to occur from i-paraffins and naphthenes.

Table 22. Advantages and disadvantages of naphtha fractions for catalytic reforming feed.

Naphtha	Fractions	+	-
Synthetic Naphtha 1	fractions 1-3	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - high fraction of C6 hydrocarbons
	fractions 4-6	+ high fraction of C7-C10 hydrocarbons + low fraction of C6 hydrocarbons	- Increasingly high fraction of aromatics in heavier fractions -low fraction of n-paraffins
Synthetic Naphtha 2	fractions 1-3	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - high fraction of C6 hydrocarbons
	fractions 4-6	+ high fraction of C7+C10 hydrocarbons + low fraction of C6 hydrocarbons	- Increasingly high fraction of aromatics in heavier fractions -low fraction of n-paraffins
Synthetic Naphtha 3	fractions 1-3	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - high fraction of C6 hydrocarbons
	fractions 4-6	+ high fraction of C7+C10 hydrocarbons + low fraction of C6 hydrocarbons	- Increasingly high fraction of aromatics in heavier fractions -low fraction of n-paraffins
Synthetic Naphtha 4	fractions 1-3	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - high fraction of C6 hydrocarbons
	fractions 4-6	+ high fraction of C7+C10 hydrocarbons + low fraction of C6 hydrocarbons in fractions 5+6	- high fraction of aromatics mainly in fraction 6 -low fraction of n-paraffins
FCC Naphtha 1	fractions 1-3	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - low fraction of naphthenes
	fractions 4-6	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - high fraction of C6 - low fraction of naphthenes
FCC Naphtha 2	fractions 1-3	+ low fraction of aromatics	- low fraction of n-paraffins - low fraction of C7-C10 hydrocarbons - high fraction of C6 hydrocarbons
	fractions 4-6	+ high fraction of C7+C10 hydrocarbons + low fraction of C6 hydrocarbons	- Increasingly high fraction of aromatics in heavier fractions - low fraction of n-paraffins - low fraction of naphthenes

As a conclusion, heavy fractions of synthetic naphthas and FCC naphtha 2 were found to be potentially suitable for catalytic reforming after intense hydrogenation. Most of the components in these fractions could be reformed to octane number boosting components, but high initial aromatics content and lack of n-paraffins reduce the

refining potential. In order to completely remove unwanted olefins from the feed, hydrogenation would have to be more intense than what the kinetic model of this thesis is suitable for. The reactions that might occur after the olefin content approaches zero are uncertain. Also there is no experimental evidence of how well the considered hydrogenation process could remove the traces of sulfur and other impurities from FCC naphtha. If catalytic reforming would be performed on naphtha in actual industrial facility, an existing reformer would likely be used, since investment cost of a new catalytic reformer is high. Typically catalytic reforming units contain their own hydrotreaters for the feed purification so it is possible that hydrogenation of naphtha could be performed with such hydrotreater to ensure feed purity.

14.4 Refinery Blending Pool Model Studies

One alternative for estimating naphtha value is to study how much it can increase the margin of refinery's gasoline production. This can be assumed to be close the maximum value that a refinery would pay for the naphtha with delivery included. This approach takes into account that naphtha can have varying value in different refinery blending pools depending on which gasoline property is restrictive. Three different refinery blending pools were studied: Gulf Coast refinery, European refinery, and Californian refinery. Value of synthetic naphthas 1–4 and FCC naphthas 1–2 were analyzed after processing scenarios 1–6. Values of products were then compared with and without estimated processing costs. Californian gasoline specifications ban the use of any other oxygenates but ethanol (Californian Code of Regulations Section 2250-2273.5, 2012). This means that etherified naphtha could not be used in Californian gasoline. However, gasoline containing ethers could be exported.

14.4.1 Optimization Method and Hypothesis of Results

Blending pool models maximization of margin was identified as smooth nonlinear optimization problem. Difficulty of non-linear optimization problems compared to linear ones is that no algorithm can solve every nonlinear optimization problem (Hillier and Liebermann 2001). GRG Nonlinear algorithm was selected from Excel 2010 Solver-tool as it was the best one available.

First all three blending pools were optimized without the studied naphthas. Results were analyzed to discover which properties are restricting the blending in each refinery.

Properties were considered to limit the blending if their values were at maximum or minimum value in one or more gasoline product. The following observations were made:

- Gulf Coast refinery is limited by vapor pressure and octane number in all products and by benzene content in US RFG regular product.
- European refinery is restricted by vapor pressure, sulfur, and oxygen in Euro 5 95 E5. It is also notable that European refinery can spend almost all of its blending components to gasoline products before the production is limited by gasoline property limits.
- Californian refinery is restricted by sulfur, vapor pressure, octane number, and oxygen for all gasoline and by aromatics content and olefin content in CaRFG premium.

The effect of hydrogenation and etherification on naphtha properties was simulated. The general trend of both processing method's effects on properties are listed in Table 23.

Table 23. Effect of hydrogenation and etherification on naphtha properties.

	RON	MON	AKI	RVP	Olefins	Oxygen
Hydrogenation	-	++	+	+	- - -	0
Etherification	+	+	+	- -	-	+

+++	significant increase
++	moderate increase
+	slight increase
0	no effect
-	slight derease
- -	moderate decrese
- - -	significant decrease

By combining the analysis of Table 23 to observations made of limiting properties in each blending pool model, hypothesis was formed on how each processing method could affect blending pool profitability compared to a case without any processing of naphtha. This hypothesis is shown in Table 24 and it indicates that etherification should have moderate to strong positive effect on profitability while the effect of hydrogenation should be small.

Table 24. Hypothesis of hydrogenation's and etherification's effect on naphtha value.

	Hydrogenation	Etherification
Gulf Coast Refinery	0	+++
European Refinery	-	++
Californian Refinery	+	++

+++	significant positive effect
++	moderate positive effect
+	slight positive effect
0	no effect
-	slight negative effect

14.4.2 Results of Blending Pool Studies

Increase in profit for each refinery and processing case was studied by optimizing the refinery profit with an optimizing algorithm. Each naphtha was studied with and without estimated processing costs and the results are presented in APPENDIX 10.

Californian refinery seemed to clearly follow the behavior expected by the hypothesis with synthetic naphtha 1 and FCC naphtha 2. Otherwise the results were disturbed by inconsistent spikes in expected naphtha value with random processing scenarios. This phenomenon was related to optimization results where the optimization algorithm found optimal solution with notably higher total gasoline production. Suggested explanation to this is that in most cases the optimization algorithm had not found global maximum for the profit, but instead a local maximum (see Figure 20). The optimization algorithm could have struggled with Californian refinery case, because blending in that case was restricted by so many properties. Either better initial values for variables or more suitable optimization algorithm could have been needed. However if the results with synthetic naphtha 1 and FCC naphtha 2 can be regarded trustworthy, etherification or combination of etherification and hydrogenation would seem to significantly increase naphtha value even after the estimated processing costs were taken into account.

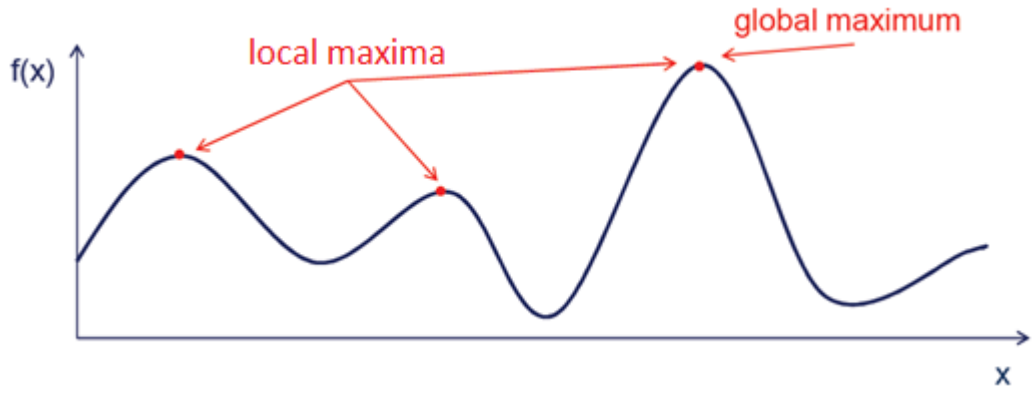


Figure 20. This figure demonstrates the difference of local and global maximum with a function f(x) dependent on single variable x (Zakharov 2012).

Studies with Gulf Coast refinery did not seem to confirm the hypothesis of assumed naphtha value dependency of limiting properties. Neither did they seem to follow any other systematic pattern. The refining margin seemed to randomly increase or decrease when naphtha processing (hydrogenation and/or etherification) was included. Results with synthetic naphtha 2 and FCC naphtha 1 indicated that naphtha value would increase when treated with hydrogenation or etherification. The highest increase in refining margin was gained with processing scenario 6 (combination of hydrogenation and etherification). Results with synthetic naphtha 1 indicated that refining margin stays approximately the same if etherified, but crashed with any processing scenario containing hydrogenation. Results with synthetic naphtha 1, synthetic naphtha 4, and FCC naphtha 2 suggest that no treatment (scenario 1) would lead to the largest increase in refining margin. Two explanations were found plausible for the lack of systematic behavior in results. First the margin could be so sensitive on changes in one or more naphtha properties that seemingly similar naphthas could lead to very different margins when naphtha properties were modified with processing. Second the system could have been functioning similarly to Californian refinery case and optimizing algorithm found local maximums instead of global ones.

European Refinery case did not confirm the original hypothesis either. However, a correlation between naphtha properties and naphtha value was detected. Excluding FCC naphtha 1 (which significantly differs from other naphthas with its lower carbon number), value of all naphthas seemed to be inversely proportional to specific gravity of the naphtha. Possible explanation to this behavior is that European refinery blending

pool is restricted by so few properties that an increase in production profit depends almost exclusively on volume of added naphtha. Deviations in other properties are thereby meaningless. Example of this correlation with synthetic naphtha 1 is illustrated in Figure 21. Results with European refinery indicate that etherification would decrease naphtha value while hydrogenation would increase it. However the small boost in naphtha value gained with volume increase did not seem to exceed the processing costs of hydrogenation.

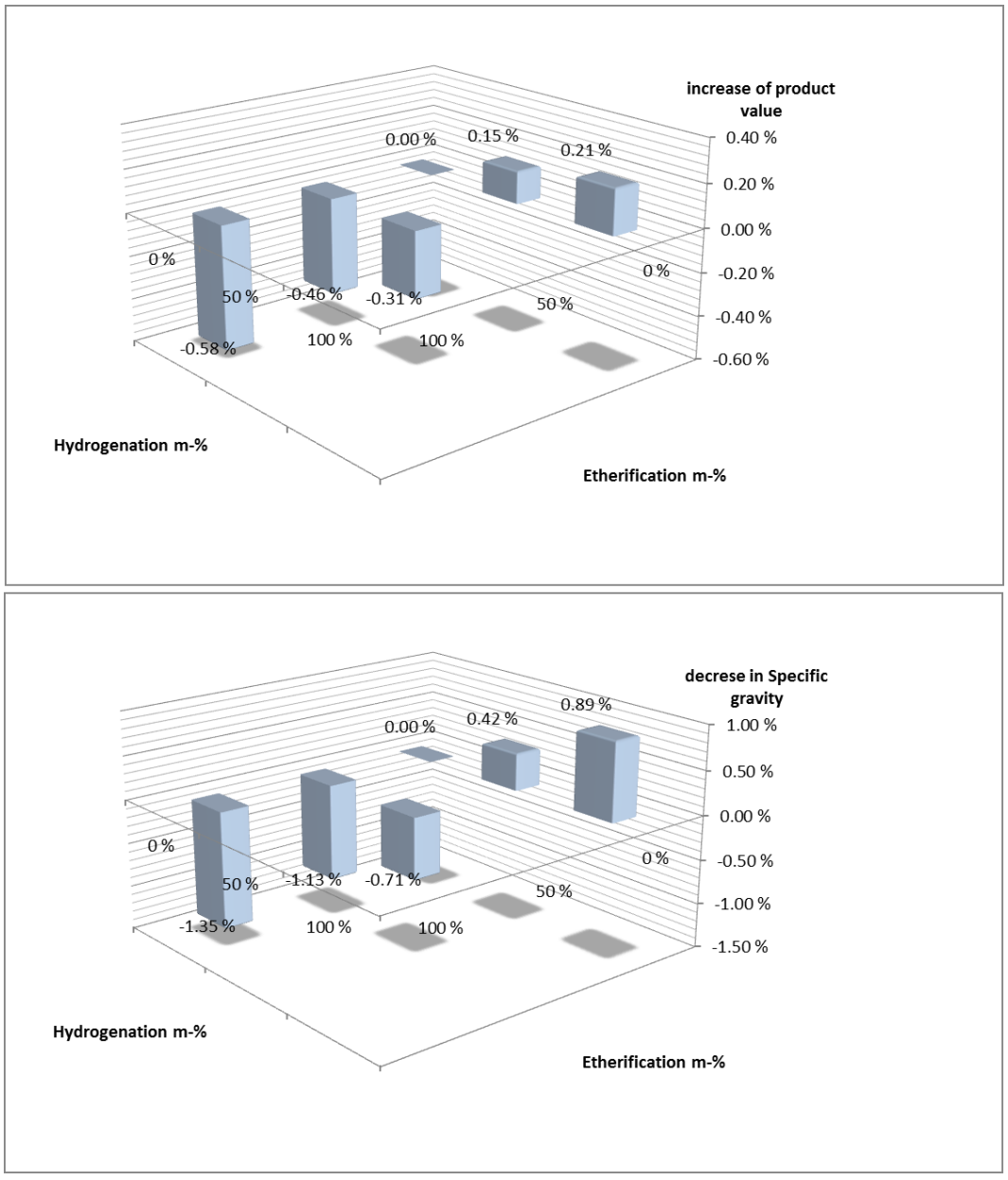


Figure 21. Decrease in specific gravity and increase in naphtha value with synthetic naphtha 1 in European Refinery.

Results of the above case study were analyzed by comparing the results with each other. Some of the results described above seemed to contain errors that were caused by unsuitable optimization algorithm, and these data sets were excluded from the following analysis. Comparison of increases in product values with different naphthas and processing scenarios are presented in Figure 22. This figure illustrates the product value increase (or decrease) with processing scenario 2–6 compared to no-treatment processing scenario (PS1). Cost of processing is taken into account in these results. Product value in European refinery model was found to depend mainly on specific gravity, which was regarded to be somewhat unrealistic in an actual refinery. Listed results from Californian refinery and Gulf Coast refinery cases indicate that processing scenarios 5 and 6 would be the most profitable though variation between result series is great.

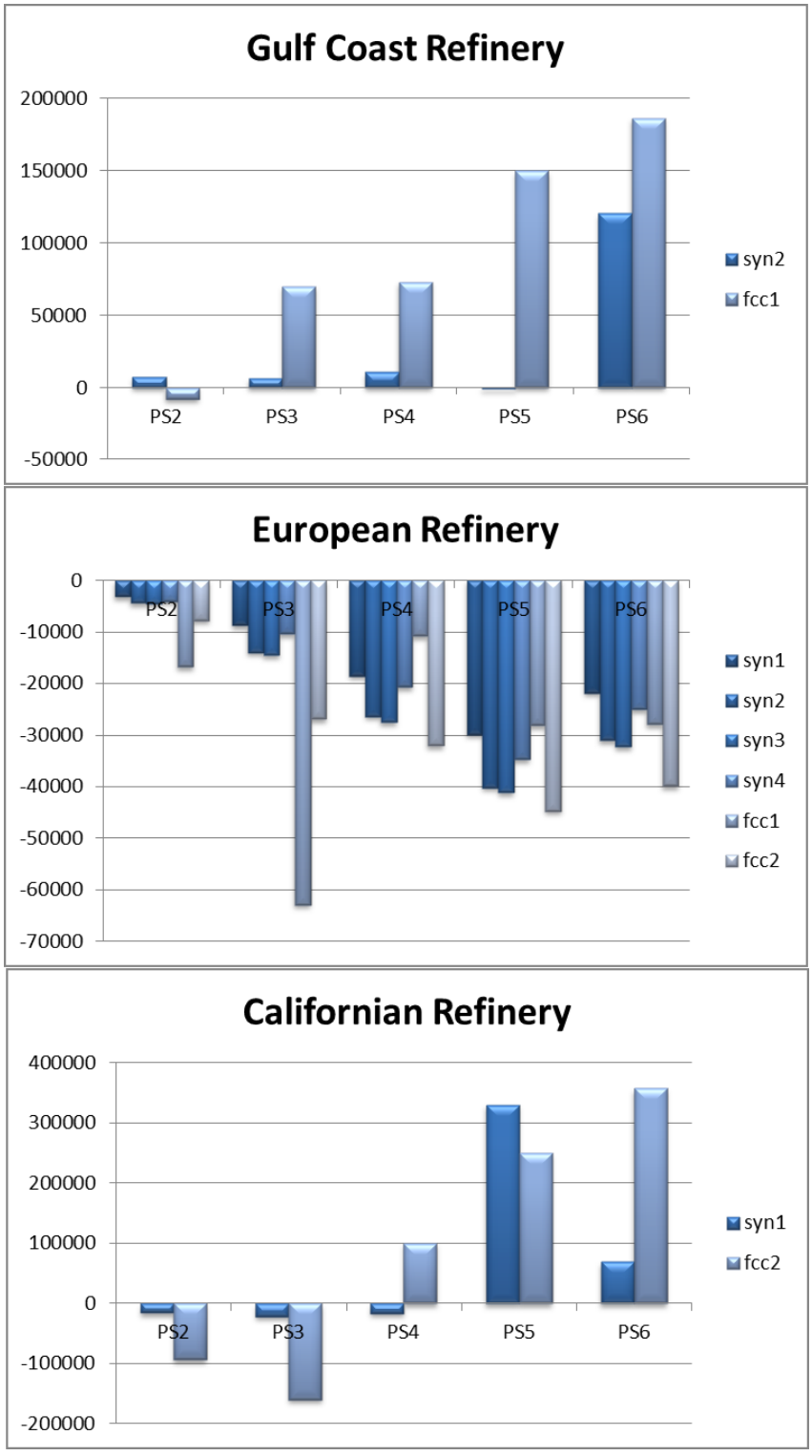


Figure 22. Increase of product value (in US $) per day with processing scenarios 2–6 in three refinery scenarios.

14.4.3 Discussion of the Results

Difficulties related to reaching global maximum values with the selected algorithm were unfortunate since they made drawing of useful conclusions from the results problematic. The same blending model was earlier used at least in two other theses (Halinen 2003, Nurmi 2007). Nurmi (2007) did not seem to have identified exactly the same problem, but Nurmi hints that there was room for improvement in consistency of results with certain component price combinations. Halinen (2003) did neither directly state that the mentioned difficulties had occurred. However Halinen's (2003) studies were limited to studying change in single property at time (sensitivity of each property on product value). This was possibly an easier problem for optimization algorithm to solve than studying simultaneous change in many properties. Also Halinen (2003) may have unknowingly studied change in local maximum value instead of global one, but never noticed this.

Despite the problems in the optimization algorithm's performance, some conclusions were drawn from the results. Firstly the initial hypothesis of optimization results was not very well in line with the results that were achieved. It seemed that in this case drawing conclusion based only on blending pool's restricting properties was not a reliable way to estimate the effect of processing on product value. Secondly, when the results series, that were considered consistent, were analyzed, highest profitability increase appeared on average with processing scenarios 5 and 6. However, the magnitude of estimated value increase with processing scenarios 5 and 6 did not seem realistic. For example value increase with FCC naphtha 2 in processing scenario 6 would mean that value would increase from 137 US dollars per barrel to ridiculously high 217 US dollars per barrel. For comparison, the market price of MTBE was around 126 US dollars per barrel at the time of the study. A conclusion was made that the selected approach for naphtha value estimation is not very accurate and is better capable for estimating the relative change in product value than the absolute monetary value.

15 Investment Profitability

By combining information of estimated initial investment costs, operating expenses and expected operating profits, estimates of total profitability of investment were formed for evaluated processing alternatives. The subject of investment profitability was

approached with a standard method for investment cost profitability analysis, net present value method (NPV, Equation 21).

$$NPV = \sum_{t=0}^{N} \frac{R_t}{(1+i)^t} \quad (21)$$

Where,

NPV is net present value ($),

t year of cash flow,

N is life cycle of investment in years (here 3 years planning and construction, and 10 years of operation = 13 years is used for calculations),

i is discount rate, which represents similar risk investment's return rate on financial markets (here 15 % is used for calculations),

R_t net cash flow at time t ($).

Initial capital investment was assumed to be spent 15 percent on the first year, 45 percent on the second year, and rest 45 percent on the third year. Costs of operating and maintenance were based on estimations in chapter 12. The result of investment profitability analysis is presented in APPENDIX 11. Trend of the results is that NVP of processing scenarios 2–3 is negative while NVP of processing scenarios 4–6 is very positive. Due to high monetary value of etherified naphtha predicted by blending pool model, predicted NVP of processing scenarios 4-6 is very significant. However, accuracy of the used naphtha value estimation method was considered low, so the results of the NVP analysis were possibly optimistic. Since hydrogenation scenarios (processing scenarios 2-3) were analyzed also with Colonial Pipeline blendstock prices, alternative product value estimate was available. The results with hydrogenated products varied very much depending on which estimation method and naphtha was considered. On average the results indicated that NVP of hydrogenation unit investment would be negative. However positive NVP was found in two cases, which were synthetic naphtha 2 in Gulf Coast refinery with partial hydrogenation, and FCC naphtha 1 in Gulf Coast refinery with full hydrogenation.

16 Discussion of Results and Conclusions

The most significant results of this thesis and some common conclusion of the results are discussed in this chapter.

16.1 Discussion of Calculation Methods

The effects of six processing scenarios on naphtha properties were compared. Using composition based calculation methods the effects of hydrogenation and etherification on naphtha properties were estimated. Composition-based approach to property calculations was found to be useful and the same methods are likely applicable in other similar studies. In this work they enabled studying the effects of naphtha processing on properties without expensive and time consuming laboratory experiments. Especially the octane calculation model (subchapter 9.6.1), was found to show potential for further use and development. Combination of Ghosh et al. (2006) nonlinear octane number model and a pseudo-component model seemed to be flexible and an accurate way to estimate octane numbers of complex mixtures. Accuracy of the method was tested by comparing calculated octane number values to measured values from literature with satisfying results.

The kinetic model of selective hydrogenation was combined of data from multiple sources, so some uncertainty of its accuracy definitely exists. However, since the main parameters were based on measured data from reaction studies, the model is assumed to be reasonably reliable. If such hydrogenation process was decided to be designed and constructed, a confirmed kinetic model is likely necessary. The etherification process was modelled with a conversion based model. Although the model is simple, it was considered quite reliable, since it was based on data from actual industrial-scale units. More likely source of error was considered to be the estimation of reactive olefin contents. As a conclusion, both models were found to be reasonably accurate considering the purposes of this work.

16.2 Properties of the Studied Naphthas

Six different olefinic naphthas, four synthetic naphthas and two FCC naphthas, were studied in this work. Their properties were found to be mainly quite similar to other typical gasoline blending components except olefin contents which were above average. Fractionation of naphthas was simulated and the content of olefins in naphtha fractions

was analyzed. Although great variance was detected, significant amount of olefins was identified in all six cuts of each naphtha. A conclusion was made that treating only a narrow cut of naphtha would not considerably reduce the total olefin content, but instead a more extensive treatment was necessary.

16.3 About Processing Alternatives

In the beginning of the study feasible layout of the overall process was considered. Feeding the etherification product into hydrogenation unit was concluded to include risk of catalyst deactivation in hydrogenation unit so this alternative was rejected. The other way around, feeding hydrogenation product to etherification was considered technically possible, but not justifiable, since hydrogenation would consume large part of olefins leaving little reactive material to etherification. By eliminating the other alternatives, a parallel layout for processing units was selected for further research.

By studying the effects of processing on different naphtha fractions, it was discovered that hydrogenation and etherification are best used for processing opposite boiling fractions of the feed. This finding is important, since it shows that etherification and hydrogenation have synergy as parallel processing methods for olefinic naphtha. It also shows which fractions are primary choices for hydrogenation or etherification, if only one processing unit is selected. Based on modelled processing effects on product properties heavier naphtha cuts were clearly the best choice for hydrogenation unit feed while lighter fractions were found to be the best alternative for etherification feed. Anyhow, it is worth noticing that these observations concern the general situation of olefinic naphtha hydrogenation and etherification and depending on details of an actual feed composition, even a narrower optimal naphtha cut can likely be defined for the units.

Since the property calculation methods and reaction models were considered to be reasonably accurate, the results from processing studies were found to be rather reliable. Some models, such as Reid vapor pressure model and distillation curve model, included simplifications related to ideal behavior of mixtures. In case of methyl-ethers these simplifications have surely caused some error, but methyl-ether contents in the studied mixtures were quite low so the inaccuracy was likely in acceptable level for this type of study.

16.4 Estimation of Naphtha Value and Investment Profitability

Properties of processed and unprocessed naphthas were compared to Colonial Pipeline's specifications in subchapter 14.2. All naphthas (processed or unprocessed) seemed to fulfill the loosely specified L-grade, so no matter which processing alternative is selected, product transportation with colonial pipeline is not out of question. However, etherification disables all BOB-grades, since oxygen is not allowed. Also neither of the studied FCC naphthas could as such or as processed fulfill the BOB-grade requirements. The most relevant information about naphtha values in Colonial Pipeline blendstock markets was reached by analyzing naphtha value with some typical blending components to supplement naphtha properties. This analysis only concerned hydrogenation products since etherification did not come into question due to oxygenate prohibition in the product specification. As a result none of the processing scenarios seemed to increase the product value enough to justify the investment in such a process. This supported the view that processing scenarios with only a hydrogenation unit are not profitable processing alternatives.

Since catalytic reforming was considered as a possible post-treatment method, convenience of the olefinic naphthas for catalytic reforming feed was analyzed. The possibility to feed the naphtha in catalytic reforming was considered to have an indirect positive effect on the naphtha value. The lightest naphtha (FCC naphtha 1) was found to be very poor alternative for catalytic reforming, since it was simply too light to form aromatics. All of other naphthas were also found to be suboptimal feed for catalytic reforming mainly because of the lack of n-paraffins. However, all naphthas contained some fractions that appeared to be somewhat appropriate for catalytic reforming feed, but intensive saturation of olefins would be necessary. Some uncertainty was related to these results since contents of some catalyst poisons in the naphthas were unknown.

Naphtha value was estimated using a blending pool model -based method. This method was found to involve difficulties related to analyzing naphtha value, since there was uncertainty whether the optimizing algorithm had actually located the global optimal solution. Also the naphtha value that model suggested was observed to be quite sensitive to how other blending component prices were determined. Since estimating blending component's absolute monetary value is difficult, this model can give results that are inaccurate. Because of these concerns the method could not be considered to

be very precise. For the aforementioned reasons, analyzing whether hydrogenation or etherification increases product value enough to justify processing, could not be fully concluded. However, there were indications that etherification would have more beneficial effects on product value than hydrogenation, since the majority of studied naphthas showed best results with etherification scenarios or combination of hydrogenation and etherification. Also since hydrogenation product values were studied with alternative method (the comparison to Colonial Pipeline's products and market prices) and similar results were gained with both methods, the results from blending pool model seem to mirror at least approximately the real market values.

Initial investment costs of processing scenarios were estimated using synthetic naphtha 2 as an example. This analysis indicated that etherification unit would cost approximately 2.5 times as much as hydrogenation unit and that the most expensive configurations would be a combination of hydrogenation and etherification (processing scenario 6) and a full etherification (processing scenario 5). Profitability of total investment was also analyzed with NPV method. Since the accuracy of product value estimates was considered fairly low, the results of total investment profitability analyzes were also likely somewhat inaccurate. Some evidence was found that hydrogenation unit could be profitable investment with certain naphthas (synthetic naphtha 2 and FCC naphtha 1). On the other hand all other hydrogenation cases seemed to have negative NPV, so mere hydrogenation alone did not seem to be a good processing alternative. According to NPV analyzes, etherification scenarios (processing scenarios 4-6) would seem to be extremely profitable investments. This result is largely based on data from blending pool models, which were possibly giving somewhat inaccurate values to naphtha. Therefore this result was taken with a bit of caution.

17 Summary

This research revealed relevant information about the study subjects, though some challenges were faced related to accuracy of product value estimations. The selected set of composition based property calculation methods, which was found to be practical tool for analyzing effect of processing with minimal initial information, is likely to be a useful aid for other similar studies. The analysis of processing effects on product properties revealed which naphtha treatments can be considered potentially feasible.

Product comparison with Colonial Pipeline specifications and catalytic reforming feed requirements revealed important dependencies between the selected processing scenarios and product suitability to the mentioned uses. Finally, analysis of investment costs together with product value estimations provided observations about expected overall profitability of studied processes.

In order to more accurately examine profit of studied processing scenarios, appropriate value estimation method would be needed. This research revealed some possible flaws in Halinen's (2002) blending pool model approach. If blending pool based value estimation method is used, optimization method must be improved. Simplifying the blending problem as a linear model might be a worthwhile approach, since this would make finding the optimal solution a lot easier. When approximate global maximum is found, more precise results could be sought with a nonlinear model.

Even though the estimation of product value was considered inaccurate, the results with investment profitability analysis showed so good results that etherification or combined etherification and hydrogenation of olefinic naphthas appeared to be very promising processing alternative. On the other hand processing scenarios with only hydrogenation unit did not seem to be profitable investments. In order to gain more information about profitability of etherification and hydrogenation + etherification processing scenarios, further studies with an improved naphtha value estimation method is suggested.

Reference List

Ali, M., Ali, S., and Siddiqui, M. (2007) 'An Appraisal of Hydrocarbons Conversion Reactions During Naphtha Reforming Process', *Petroleum Science and Technology*, 25, 1321-1331.

Ali, S. and Al-Baghli, N. (2004) 'Overview of FCC gasoline post-treating technologies', *Annual Catalysts in Petroleum Refining and Petrochemicals Symposium Papers*, 61-74.

Antos, G., Aitani, A., and Parera, J. (1995) *Catalytic Naphtha Reforming Science and Technology*, New York: Marcel Dekker inc.

Argus Media (2010) 'Methodology and Specifications Guide', available: http://www.cftc.gov/ucm/groups/public/@swaps/documents/dfsubmission/dfsubmissionmult_092810-argus4.pdf [accessed 29 Mar 2014].

Argus Media (2014), *Argus US Products,* Issue 14E-054 / Thursday 20 March 2014, London: Argus Media.

ASTM (1971) *Physical Constants of Hydrocarbons C_1 to C_{10},* Baltimore: ASTM Data Series Publication DS 4A.

ASTM International Standard (1999) *Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)*, D 323 – 99a.

Audibert, F. (2006) *Waste Engine Oils - Refining and Energy Recovery*, Elsevier [online], available: http://app.knovel.com/hotlink/toc/id:kpWEORER01/waste-engine-oils-rerefining [accessed 11 Jan 2014].

Baird, C. (1989) *Guide to Petroleum Product Blending,* Austin, Texas: HPI Consultants.

Bergius, F. (1932) 'Chemical reactions under high pressure', Nobel Lecture, 21 May 1932, available: http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1931/bergius-lecture.pdf [accessed 12 May 2014].

Blencoe, G (2009) ' Cost of hydrogen from different sources', *Hydrogen Car Revolution* [online], 9 Nov, available: http://www.h2carblog.com/?p=461 [accessed 4 Mar 2014].

Bloch, H. (2006) *Compressors and Modern Process Applications,* John Wiley & Sons [online], available: http://app.knovel.com/hotlink/toc/id:kpCMPA0003/compressors-modern-process [accessed 1 Feb 2014].

Brunet, S., Mey, D., Pérot, G., Bouchy, C. and Diehl, F. (2005) 'On hydrodesulfurization of FCC gasoline: a review', *Applied Catalysis A: General*, 278, 143-172.

Californian Air Resources Board - Californian Code of Regulations Section 2250-2273.5 of 9 October 2012 on the Californian reformulated gasoline regulations.

Chase, J., Woods, H., and Kennedy, B., Gulf Canada Limited (1980) *Preparation of Gasoline Containing Tert-amyl Methyl Ether*, U.S. Pat. 4,193,770.

Chen, D., Moljord, K., Holmen, A. (2012) 'A methanol to olefins review: Diffusion, coke formation and deactivation on SAPO type catalysts', *Microporous and Mesoporous Materials*, 164, 239–250.

Colonial Pipeline Company (2008) *Colonial Pipeline Company Home Page* [online], available: http://www.colpipe.com/ [accessed 5 Jan 2014].

Colonial Pipeline Company (2013) *Rules and Regulations Tariff Governing the Transportation of Petroleum Products*, FERC 98.12.0 available: http://www.colpipe.com/pdfs/FERC%2098.12.0%20_%20Rules%20and%20Regulations%20Tariff.pdf [accessed 28 Dec 2013].

Commission Directive (EU) 2011/63/EU of 1 June 2011 amending, for the purpose of its adaptation to technical progress, Directive 98/70/EC of the European Parliament and of the Council relating to the quality of petrol and diesel fuels.

Digital Refining (2010) *Catalytic reforming options and practices* [online], available: http://www.digitalrefining.com/article/1000479,Catalytic_reforming_options_and_practices.html#.UvDS_fmSyE5 [accessed 29 Dec 2013].

Directive (EC) 2009/30/EC of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC.

Directive (EC) 98/70/EC of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC.

EIA (2014) *Electric Power Monthly*, available: http://www.eia.gov/electricity/monthly/epm_table_grapher.cfm?t=epmt_5_6_a [accessed 4.3.2014].

EN Standards (2008) *Automotive fuels. Unleaded petrol. Requirements and test methods*, EN 228:2008.

EN Standards (2012) *Automotive fuels. Unleaded petrol. Requirements and test methods*, EN 228:2012.

Exxon Mobil (2014) *Methanol to Gasoline (MTG) Production of Clean Gasoline from Coal* [Brochure], available: http://www.exxonmobil.com/Apps/RefiningTechnologies/files/sellsheet_09_mtg_brochure.pdf [accessed: 19 May 2014].

Fahim, M., Alsahhaf, T. and Elkilani, A. (2010) *Fundamentals of Petroleum Refining*, Elsevier [online], available: http://app.knovel.com/hotlink/toc/id:kpFPR00003/fundamentals-petroleum [accessed 31.12.2013].

Faiz, A., Weaver, C., Walsh, M. (1996) *Air Pollution from Motor Vehicles: Standards and Technologies for Controlling Emissions*, Washington: World Bank Publications.

Fan, Y., Bao, X. and Shi, G. (2005) 'Hβ/HZSM-5 composite carrier supported catalysts for olefins reduction of FCC gasoline via hydroisomerization and aromatization', *Catalysis Letters,* 105, 67–74.

Fan, Y., Lin, X., Shi, G., Liu, H. and Bao, X. (2007) 'Realumination of dealuminated HZSM-5 zeolite by citric acid treatment and its application in preparing FCC gasoline hydro-upgrading catalyst', *Microporous and Mesoporous Materials*, 98, 174–181.

Fan, Y., Yin, J., Shi, G., Liu, H., Gao J., and Bao X. (2009a) 'A Six-Lump Kinetic Model for Olefin Hydrogenation, Hydroisomerization and Aromatization in FCC Gasoline Hydro-Upgrading', *Catalysis Letters*, 129 (1), 181–188.

Fan, Y., Yin, J., Shi, G., Liu, H., Gao J., and Bao X. (2009b) Mechanistic Pathways for Olefin Hydroisomerization and Aromatization in Fluid Catalytic Cracking Gasoline Hydro-upgrading, *Energy & Fuels*, 23, 3016–3023.

Fan, Y., Shi, G., and Bao, X. (2013) 'A Process for Producing Ultraclean Gasoline by Coupling Efficient Hydrodesulfurization and Directional Olefin Conversion', *American Institute of Chemical Engineers Journal*, 59 (2), 571–581.

Financial Post (2011), 'Enbridge, Caisse snap up Conoco pipelines', available: http://business.financialpost.com/2011/11/16/enbridge-caisse-snap-up-conoco-pipelines/?__lsa=3562-9136 [accessed 12 March 2014].

Ghosh, P., Hickey K., and Jaffe, J. (2006) 'Development of a Detailed Gasoline Composition-Based Octane Model', *Industrial & Engineering Chemistry Research*, 45, 337–345.

Ghosh, P., Andrew, A., Quann, R., and Halbert, T., (2009) 'Detailed Kinetic Model for the Hydro-desulfurization of FCC Naphtha', Energy Fuels, 23, 5743–5759.

Girgis M. and Gates, B. (1991) 'Reactivities, Reaction Networks, and Kinetics in High-pressure Catalytic Hydroprocessing', *Industrial & Engineering Chemistry Research*, 30, 2021–2058.

Haldor Topsoe (2014) *TIGAS Technology for gasoline production* [Brochure], available: http://www.exxonmobil.com/Apps/RefiningTechnologies/files/sellsheet_09_mtg_brochure.pdf [accessed 17 May 2014].

Halinen, S. (2003) *Comparison of Processes for Clean Fuels Production*, Master's Thesis (MSc), Helsinki University of Technology.

Hillier, F. and Lieberman, G. (2001) *Introduction to Operations Research,* Seventh Edition, New York: McGraw-Hill Higher Education.

Ho, T. (2008) 'Kinetic Modeling of Large-Scale Reaction Systems', *Catalysis Reviews: Science and Engineering*, 50 (3), 287–378.

International Council on Clean Transportation (2014) *Policy Update - China V Gasoline and Diesel Fuel Quality Standards*, January 2014, Beijing, Berlin, Brussels, San Francisco, Washington: International Council on Clean Transportation (ICCT).

Leprince, P. (2001) *Petroleum Refining, Volume 3 - Conversion Processes,* Editions Technip [Online], available: http://app.knovel.com/hotlink/toc/id:kpPRVCP002/petroleum-refining-volume [accessed 14 May 2014].

Lurgi (2014) Methanol-to-propylene – Lurgi MTP process [Brochure], available: http://www.engineering-solutions.airliquide.com/file/otherelementcontent/pj/42/9e/ec/af/methanol-to-propylene%20flyer5517811988317851881.pdf [accessed 17 May 2014].

Mall, I. (2013) 'Lecture 6: Catalytic Reforming', *Chemical Technology (Organic)* [online], available: http://nptel.ac.in/courses/103107082/module6/lecture6/lecture6.pdf [accessed 29 Apr 2014].

Maples, R. (2000) *Petroleum Refinery Process Economics (2nd Edition)*, PennWell [Online], available at: http://app.knovel.com/hotlink/toc/id:kpPRPEE001/petroleum-refinery-process [accessed 16.1.2014].

Marcilly, C. (2006) *Acido-Basic Catalysis, Volume 2 - Application to Refining and Petrochemistry*, Editions Technip [online], available: http://app.knovel.com/hotlink/toc/id:kpABCVARPE/acido-basic-catalysis [23 Dec 2013].

McGraw Hill Financial (2014), *Platts US Marketscan,* Volume 40 / Issue 55 / March 21, 2014, New York: McGraw Hill Financial.

McGraw Hill Higher Education (2003), 'Equpment Costs' [online], available: http://www.mhhe.com/engcs/chemical/peters/data/.

Methanex (2014) *Methanol Price* [online], available: http://www.methanex.com/products/methanolprice.html [accessed 13 Apr 2014].

Neste Jacobs (2014) Technologies & Products [online], available: http://www.nestejacobs.com/index.php?page=13&lang=en [accessed 1 Aug 2014].

Nurmi, P. (2007) *Eksotermisen Irreversiibelin Prosessin Hallinta*, Master's Thesis (MSc), Helsinki University of Technology.

Ocaranza, E., Gonzáleza, H. and Ramírez J. (2004) 'Hydroconversion of model mixtures of FCC gasoline over metal–zeolite catalysts. Reaction study and mathematical modelling', *Chemical Engineering Science*, 59, 5679–5685.

Olsbye, U., Svelle, S., Bjørgen, M., Beato, P., Janssens, T., Joensen, F., Bordiga, S. and Lillerud, K. (2012) 'Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity', *Angewandte Reviews*, 51, 5810–5831.

Phillips, S., Tarud, J., Biddy, M. and Abhijit Dutta (2011) 'Gasoline from Woody Biomass via Thermochemical Gasification, Methanol Synthesis, and Methanol-to-Gasoline

Technologies: A Technoeconomic Analysis', *Industrial & Engineering Chemistry Research*, 50, 11734–11745.

Peng, D.-Y. and Robinson D. (1976) 'A New Two-Constant Equation of State', *Industrial and Engineering Chemistry Fundamentals*, 15 (1), 59–64.

Rantakylä, T.-K., Toppinen, S., Salmi, T. and Aittamaa, J. (1996) 'Investigation of the Hydrogenation of Some Substituted Alkylbenzenes in a Laboratory Scale Trickle-Bed Reactor', *Journal of Chemical Technology & Biotechnology*, 67 (3), 265–275.

Rase, H. (2000) *Handbook of Commercial Catalysts - Heterogenous Catalysts*, CRC Press LLC.

Rizvi, S. (2009) *Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design*, ASTM International [Online], available: http://app.knovel.com/hotlink/toc/id:kpCRLCTSD1/comprehensive-review.

Rothaemel, M., Finck, U., Renner, T. and Buchold H. (2011) *Process and Plant for Producing C2-C4 Olefins from Methanol and/or Dimethyl Ether with Increased Yield*, US Patent 20110319686 A1.

Sadeghbeigi, R. (2012) *Fluid Catalytic Cracking Handbook - An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units (3rd Edition),* Elsevier [online], available: http://app.knovel.com/hotlink/toc/id:kpFCCHAEG2/fluid-catalytic-cracking [accessed 29 Dec 2013].

Schreiner, M. (1978) *Research Guidance Studies to Assess Gasoline from Coal by Methanol-to-Gasoline and Sasol-Type FischerTropsch Technologies,* U.S. Department of Energy: Washington, DC.

Shorey, S., Lomas, D. and Keesom, W. (1999) 'Use FCC feed pretreating methods to remove sulfur', *Hydrocarbon Processing*, Nov, 43–51.

Surinder, P. (2003) *Refining Processes Handbook*, Elsevier [online], available: http://app.knovel.com/hotlink/toc/id:kpRPH00005/refining-processes-handbook [accessed 18 Dec 2013].

Toppinen, S., Rantakylä, T.-K., Salmi, T. and Aittamaa, J. (1996a) 'Kinetics of the Liquid Phase Hydrogenation of Di- and Trisubstituted Alkylbenzenes over a Nickel Catalyst', *Industrial & Engineering Chemistry Research*, 35 (12), 4424–4433.

Toppinen, S., Rantakylä, T.-K., Salmi, T. and Aittamaa, J. (1996b) 'Kinetics of the Liquid-Phase Hydrogenation of Benzene and Some Monosubstituted Alkylbenzenes over a Nickel Catalyst', *Industrial & Engineering Chemistry Research*, 35 (6), 1824–1833.

TransportPolicy.net (2014), 'China: Fuels: Diesel and Gasoline', available: http://transportpolicy.net/index.php?title=China:_Fuels:_Diesel_and_Gasoline [accessed 14 March 2014].

UOP (2014), 'Merox Treating', available: http://www.uop.com/products/catalysts/treating/ [accessed 14 March 2014].

UOP (2013) A different game plan [Brochure], available: http://www.uop.com/wp-content/uploads/2013/12/Methanol-to-Olefins-Technology_Hydrocarbon-Engineering-Dec-2013.pdf.

U.S. Department of Energy (2012), *Hydrogen Production Cost Using Low-Cost Natural Gas*, Record number: 12024, available: http://hydrogen.energy.gov/pdfs/12024_h2_production_cost_natural_gas.pdf [accessed 22 Mar 2014].

Utah Valley University (2013), 'Heat of Hydrogenation' http://science.uvu.edu/ochem/index.php/alphabetical/g-h/heat-of-hydrogenation/ [accessed 28 May 2014].

Viswanadham, N., Negi, B., Garg, M., Sundaram, M., Sairam, B. and Agarwal, A. (2007) 'Reformulation of FCC gasoline', *Fuel*, 86, 1290–1297.

Zakharov, A. (2012) 'Lecture 9: Nonlinear Programming', *Basics in Production Planning and Control* [online], available: https://noppa.aalto.fi/noppa/kurssi/ke-90.2500/luennot/KE-90_2500_nonlinear_programming.pdf [accessed 12 May 2014].

APPENDIX 1

Colonial Pipeline Company's blendstock product specifications after blending with 10 vol-% of ethanol

Grade	Long Name	Min RON	Min MON	Min (RON+MON)/2	Max Oxygen Content (wt-%)	Max MTBE (vol-%)	Max RVP (psi)*	Max sulfur (ppmwt)	Max Benzene (vol-%)	Max Aromatics content (vol-%)	Max Olefin Content (vol-%)
Grade A	CBOB - 87 Octane after blending with 10% denatured fuel Ethanol	-	82.0	87.0	0.1	0.25	8.8–15.5	80	3.8	-	-
Grade D	CBOB - 93 Octane after blending with 10% denatured fuel Ethanol	-	-	93.0	0.1	0.25	8.8–15.5	80	3.8	-	-
Grade F	RBOB - 87 Octane after blending with 10% denatured fuel Ethanol	-	82.0	87.0	0.0	0.25	9.0–15.0	80	1.30	50	25
Grade H	RBOB - 93 Octane after blending with 10% denatured fuel Ethanol	-	-	93.0	0.0	0.25	9.0–15.0	80	1.30	50	25
Grade S	Atlanta CBOB - 87 Octane after blending with 10% denatured fuel Ethanol	-	82.0	87.0	0.1	0.25	8.0–14.5	80	3.8	-	-
Grade T	Atlanta CBOB - 93 Octane after blending with 10% denatured fuel Ethanol	-	-	93.0	0.1	0.25	8.0–14.5	80	3.8	-	-

*Maximum RVP has varying value in different subgrades. Transportation of subgrades depends on area and season adapting the gasoline vapor pressure limit changes.

Conversion of pseudo-components to Aspen Plus components

Pesudo-component	**Aspen Plus component**
n-paraffins:	
C3	PROPANE
C4	N-BUTANE
C5	N-PENTANE
C6	N-HEXANE
C7	N-HEPTANE
C8	N-OCTANE
C9	N-NONANE
C10	N-DECANE
i-paraffins:	
C4	ISOBUTANE
C5	2-METHYL-BUTANE
	2,2-DIMETHYL-PROPANE
C6	2-METHYL-PENTANE
	3-METHYL-PENTANE
	2,2-DIMETHYL-BUTANE
	2,3-DIMETHYL-BUTANE
C7	2-METHYLHEXANE
	3-METHYLHEXANE
	3-ETHYLPENTANE
	2,2-DIMETHYLPENTANE
	2,3-DIMETHYLPENTANE
	2,4-DIMETHYLPENTANE
	3,3-DIMETHYLPENTANE
	2,2,3-TRIMETHYLBUTANE
C8	2-METHYLHEPTANE
	3-METHYLHEPTANE
	4-METHYLHEPTANE
	3-ETHYLHEXANE
	2,2-DIMETHYLHEXANE

…CONTINUED	
	2,2-DIMETHYLHEXANE
	2,3-DIMETHYLHEXANE
	2,4-DIMETHYLHEXANE
	2,5-DIMETHYLHEXANE
	3,3-DIMETHYLHEXANE
	3,4-DIMETHYLHEXANE
	2-METHYL-3-ETHYLPENTANE
	3-METHYL-3-ETHYLPENTANE
	2,2,3-TRIMETHYLPENTANE
	2,2,4-TRIMETHYLPENTANE
	2,3,3-TRIMETHYLPENTANE
	2,3,4-TRIMETHYLPENTANE
	2,2,3,3-TETRAMETHYLBUTANE
C9	2,6-DIMETHYLHEPTANE
C10	2,5-DIMETHYLOCTANE
olefins:	
C4	1-BUTENE
	CIS-2-BUTENE
	TRANS-2-BUTENE
	ISOBUTYLENE
C5	1-PENTENE
	CIS-2-PENTENE
	TRANS-2-PENTENE
	2-METHYL-1-BUTENE
	3-METHYL-1-BUTENE
	2-METHYL-2-BUTENE
C6	1-HEXENE
	CIS-2-HEXENE
	TRANS-2-HEXENE
	CIS-3-HEXENE
	TRANS-3-HEXENE
	2-METHYL-1-PENTENE
	3-METHYL-1-PENTENE

….CONTINUED	
	4-METHYL-1-PENTENE
	2-METHYL-2-PENTENE
	3-METHYL-CIS-2-PENTENE
	3-METHYL-TRANS-2-PENTENE
	4-METHYL-CIS-2-PENTENE
	4-METHYL-TRANS-2-PENTENE
	2-ETHYL-1-BUTENE
	2,3-DIMETHYL-1-BUTENE
	3,3-DIMETHYL-1-BUTENE
	2,3-DIMETHYL-2-BUTENE
C7	1-HEPTENE
	CIS-2-HEPTENE
	TRANS-2-HEPTENE
	CIS-3-HEPTENE
	2-METHYL-1-HEXENE
	3-METHYL-1-HEXENE
	4-METHYL-1-HEXENE
	5-METHYL-1-HEXENE
	2-ETHYL-1-PENTENE
	3-ETHYL-1-PENTENE
	2,3,3-TRIMETHYL-1-BUTENE
C8	2,3-DIMETHYL-1-HEXENE
C9	2-METHYL-1-OCTENE
C10	2-METHYL-1-NONENE
naphthenes:	
C5	CYCLOPENTANE
C6	METHYLCYCLOPENTANE
	CYCLOHEXANE
C7	ETHYLCYCLOPENTANE
	1,1-DIMETHYLCYCLOPENTANE
	CIS-1,2-DIMETHYLCYCLOPENTANE
	TRANS-1,2-DIMETHYLCYCLOPENTANE
	TRANS-1,3-DIMETHYLCYCLOPENTANE

….CONTINUED	
	METHYLCYCLOHEXANE
C8	N-PROPYLCYCLOPENTANE
	ISOPROPYLCYCLOPENTANE
	1-METHYL-1-ETHYLCYCLOPENTANE
	1,1,2-TRIMETHYLCYCLOPENTANE
C9	ISOPROPYLCYCLOHEXANE
C10	ISOBUTYLCYCLOHEXANE
Cyclo-olefins:	
C5	CYCLOPENTENE
C6	1-METHYLCYCLOPENTENE
	3-METHYLCYCLOPENTENE
	4-METHYLCYCLOPENTENE
	CYCLOHEXENE
C7	CYCLOHEPTENE
C8	VINYLCYCLOHEXENE
C9	1-METHYL-4-VINYLCYCLOHEXENE
aromatics:	
C6	BENZENE
C7	TOLUENE
C8	ETHYLBENZENE
	O-XYLENE
	M-XYLENE
	P-XYLENE
C9	N-PROPYLBENZENE
	ISOPROPYLBENZENE
	1-METHYL-2-ETHYLBENZENE
	1-METHYL-3-ETHYLBENZENE
	1-METHYL-4-ETHYLBENZENE
	1,2,3-TRIMETHYLBENZENE
	1,2,4-TRIMETHYLBENZENE
	1,3,5-TRIMETHYLBENZENE
C10	ISOBUTYLBENZENE
C11	1-ETHYL-2-ISOPROPYLBENZENE

Bleding pools of studied refinery scenarios. ∞-sign means that the component was assumed to be excessively available on the market.

Gulf Coast Refinery	N-butane	LSR	Reformate	Full Range FCC gasoline	Ethanol	Toluene	MTBE	Alkylate
Capacity bbl/d	∞	38 000	54 000	76 000	∞	∞	∞	14 000
RON	95.5	67.9	99.3	87	124	120.1	118	94
MON	90.7	71.7	88.3	77	95	103.5	102	89.4
(RON+MON)/2	93.1	69.8	93.8	82	109.5	111.8	110	91.7
RVP, kPa	355	69	28	52	165	7	55	23
RVP, psi	51.49	10.01	4.06	7.54	23.93	1.02	7.98	3.34
Specific gravity	0.577	0.673	0.83	0.77	0.794	0.87	0.744	0.7
E70, vol-%	100	81.1	4.5	17	0	0	98	14
E95, vol-%	100	92	19	37	100	0	100	38
E100, vol-%	100	95.3	24	41	100	0	100	54
E105, vol-%	100	97	29.5	46	100	0	100	71
E150, vol-%	100	100	76.5	76	100	100	100	94
E180, vol-%	100	100	94.5	96	100	100	100	99
Sulfur, wt-ppm	2	5	2	50	0	0	5	12
Benzene, vol-%	0	0.8	0.7	0.8	0	0	0	0
Olefins, vol-%	0	0	0	20	0	0	0	0
Aromatics, vol-%	0	2	66.9	20	0	100	0	0
Oxygen, wt-%	0	0	0	0	34.8	0	18.2	0

European Refinery	N-butane	Isopentane	LSR	Isomerate	Reformate	Light FCC	Heavy FCC	Ethanol	Toluene	MTBE	Alkylate
Capacity bbl/d	∞	8 000	6 000	20 000	70 000	26 000	36 000	∞	∞	∞	18 000
RON	95.5	88.5	73	84.9	99.3	92	87	124	120.1	118	95
MON	90.7	84.8	69	81.6	88.3	81	76	95	103.5	102	91.2
(RON+MON)/2	93.1	86.65	71	83.25	93.8	86.5	81.5	109.5	111.8	110	93.1
RVP, kPa	355	142.7	64	43.3	28	60	4	165	7	55	23
RVP, psi	51.49	20.7	9.28	6.28	4.06	8.7	0.58	23.93	1.02	7.98	3.34
Specific gravity	0.577	0.624	0.68	0.699	0.83	0.67	0.8	0.794	0.87	0.744	0.7
E70, vol-%	100	100	81.1	88	4.5	70	4	0	0	98	14
E95, vol-%	100	100	92	100	19	100	30	100	0	100	38
E100, vol-%	100	100	95	100	24	100	36	100	0	100	54
E105, vol-%	100	100	97	100	29.5	100	42	100	0	100	71
E150, vol-%	100	100	100	100	76.5	100	97	100	100	100	94
E180, vol-%	100	100	100	100	94.5	100	99.8	100	100	100	99
Sulfur, wt-ppm	2	2	50	2	2	20	20	0	0	5	12
Benzene, vol-%	0	0.01	2.3	0.04	0.9	0.6	0.8	0	0	0	0
Olefins, vol-%	0	0	3	0	0	40	20	0	0	0	0
Aromatics, vol-%	0	0	3	5	66.9	1	40	0	100	0	0
Oxygen, wt-%	0	0	0	0	0	0	0	34.8	0	18.2	0

Californian Refinery	N-butane	LSR	Isomerate	Reformate	Light FCC	Medium FCC	Light hydro-crackate	Medium hydro-crackate	Ethanol	Toluene	Alkylate
Capacity	∞	6 000	12 000	48 000	16 000	46 000	12 000	20 000	∞	∞	28 000
RON	95.5	78.9	86.8	99.3	93.8	86.9	82	67	124	120.1	96.8
MON	90.7	80.7	84	88.3	81.5	77.8	80.5	66	95	103.5	92.8
(RON+MON)/2	93.1	79.8	85.4	93.8	87.65	82.35	81.25	66.5	109.5	111.8	94.8
RVP, kPa	355	90	85	34	98	20	86	10	165	7	23
RVP, psi	51.49	13.05	12.33	4.93	14.21	2.9	12.47	1.45	23.93	1.02	3.34
Specific gravity	0.577	0.673	0.652	0.83	0.734	0.806	0.701	0.721	0.794	0.87	0.7
E70, vol-%	100	81.1	94	4.5	70	4	52	0	0	0	14
E95, vol-%	100	92	100	19	100	30	98	8	100	0	38
E100, vol-%	100	95.3	100	24	100	36	100	16	100	0	54
E105, vol-%	100	97	100	29.5	100	42	100	24	100	0	71
E150, vol-%	100	100	100	76.5	100	97	100	100	100	100	94
E180, vol-%	100	100	100	94.5	100	99.8	100	100	100	100	99
Sulfur, wt-ppm	2	54	1	2	30	76	4	4	0	0	12
Benzene, vol-%	0	0.1	0.25	0.63	0.63	0.7	1	0.8	0	0	0
Olefins, vol-%	0	0.25	0	0	61.2	5.7	0.5	0.05	0	0	0.1
Aromatics, vol-%	0	0.1	0.25	68.9	1.7	23.2	1	16	0	100	0
Oxygen, wt-%	0	0	0	0	0	0	0	0	34.8	0	0

APPENDIX 4

Value of blending components and gasoline products used in optimization model.

Products or Blending Component	**Value (US Dollars per Barrel)**
Gasoline Products:	
• US RFG premium	$ 123.24
• US RFG regular	$ 114.38
• US Convetional regular	$ 111.78
• Euro 5 98 E5	$ 140.02
• Euro 5 95 E5	$ 133.74
• Euro 5 95 E10	$ 129.72
• CaRFG Premium	$ 127.15
• CaRFG Midgrade	$ 124.63
• CaRFG Regular	$ 122.11
Purchased Blending Components:	
• N-butane	$ 52.50
• Ethanol	$ 125.58
• Toluene	$ 165.27
• MTBE	$ 126.35
Produced Blending Components:	
• Isopentane	$ 56.70
• LSR	$ 72.00
• Isomerate	$ 106.67
• Reformate	$ 135.50
• Light FCC	$ 108.00
• Heavy FCC	$ 116.94
• Medium FCC	$ 112.50
• Full Range FCC	$ 108.00
• Light Hydrocrackate	$ 90.00
• Medium Hydrocrackate	$ 72.00
• Alkylate	$ 128.52

Products, reactive olefin components, and conversions for C4-C7 olefins.

Product	**Reactive Olefins**	**Conversion**
MTBE (Methyl tert-butyl ether alias 2-Methyl-2-methoxypropane)	Reactive C4 Olefins: 2-Methylpropene	99 mol-%
TAME (Tertiary amyl methyl ether alias 2-Methyl-2-methoxy butane)	Reactive C5 Olefins: 2-Methyl-2-butene 2-Methyl-1-butene	90 mol-%
THxME (Tetiary hexyl methyl ethers)	Reactive C6 Olefins: 2-Methyl-1-pentene 2-Methyl-2-pentene 3-Methyl- cis-2-pentene 3-Methyl- trans-2-pentene 2-Ethyl-1- butene 2,3-Dimethyl- 2-butene 2,3-Dimethyl-1-butene	60 mol-%
THpME (Tertiary pentyl methyl ethers)	Reactive C7 Olefins: 2-Methyl-1-hexene 2-Methyl-2-hexene 3-Methyl-cis-2-hexene 3-Methyl-trans-2-hexene 3-Methyl-cis-3-hexene 3-Methyl-trans-3-hexene 2-Ethyl-1-pentene 2,3-Dimethyl-1-pentene 2,3-Dimethyl-2-pentene 3,4-Dimethyl-cis-2-pentene 3,4-Dimethyl-trans-2-pentene 3-Methyl-2-ethyl-1-butene 2,4-Dimethyl-1 pentene 2,4-Dimethyl-2-pentene 3-Ethyl-2-pentene 2,3,3-Trimethyl-2-butene	25 mol-%

Compositions of studied naphthas

Composition (wt-%) of synthetic naphtha 1:

Carbon no.	Naph.	n-paraf.	i-Paraf.	Cyclo-Ol.	Olef.	Arom.	Total
3	-	-	-	-	-	-	-
4	-	0.01	0.13	-	0.21	-	0.35
5	0.75	1.00	12.96	0.03	3.71	-	18.45
6	4.52	0.83	10.72	0.42	4.29	0.06	20.84
7	12.90	0.51	6.54	2.23	2.74	2.44	27.35
8	2.97	0.02	0.25	6.84	1.04	12.02	23.14
9	0.38	0.01	0.08	0.69	0.29	7.10	8.56
10	0.07	-	-	-	0.15	0.95	1.17
11+	0.03	-	0.05	-	-	0.05	0.14
Total	21.61	2.38	30.73	10.21	12.43	22.63	100.00

Composition (wt-%) of synthetic naphtha 2:

Carbon no.	Naph.	n-paraf.	i-Paraf.	Cyclo-Ol.	Olef.	Arom.	Total
3	-	-	-	-	-	-	-
4	-	0.01	0.16	-	0.46	-	0.62
5	0.95	1.19	15.89	0.06	8.04	-	26.13
6	3.96	0.68	9.10	0.57	6.44	0.05	20.80
7	11.97	0.44	5.89	3.17	4.36	2.23	28.05
8	1.69	0.01	0.14	5.98	1.02	6.75	15.59
9	0.27	-	0.05	0.74	0.35	4.88	6.29
10	0.04	-	-	-	0.14	0.54	0.72
11+	0.30	0.05	0.70	-	-	0.74	1.80
Total	19.17	2.39	31.93	10.51	20.80	15.19	100.00

Composition (wt-%) of synthetic naphtha 3:

Carbon no.	Naph.	n-paraf.	i-Paraf.	Cyclo-Ol.	Olef.	Arom.	Total
3	-	-	-	-	-	-	-
4	-	0.03	0.09	-	0.48	-	0.61
5	0.50	3.28	8.36	0.04	7.85	-	20.04
6	2.84	2.56	6.53	0.57	8.58	0.07	21.15
7	7.75	1.49	3.81	2.86	5.24	2.77	23.93
8	1.46	0.05	0.12	7.22	1.63	11.22	21.70
9	0.20	0.02	0.04	0.79	0.50	7.20	8.75
10	0.04	-	-	-	0.27	1.04	1.35
11+	0.35	0.24	0.62	-	-	1.26	2.48
Total	13.14	7.68	19.57	11.49	24.55	23.57	100.00

Composition (wt-%) of synthetic naphtha 4:

Carbon no.	Naph.	n-paraf.	i-Paraf.	Cyclo-Ol.	Olef.	Arom.	Total
3	-	-	-	-	-	-	-
4	-	0.03	0.23	-	0.41	-	0.67
5	1.07	2.64	17.84	0.07	5.55	-	27.16
6	5.11	1.74	11.75	0.76	5.12	0.05	24.53
7	11.85	0.86	5.83	3.25	2.66	1.66	26.11
8	1.91	0.02	0.16	6.98	0.71	5.74	15.52
9	0.23	0.01	0.05	0.66	0.18	3.15	4.27
10	0.04	-	-	-	0.08	0.39	0.51
11+	0.25	0.08	0.51	-	-	0.40	1.23
Total	20.45	5.38	36.36	11.71	14.71	11.40	100.00

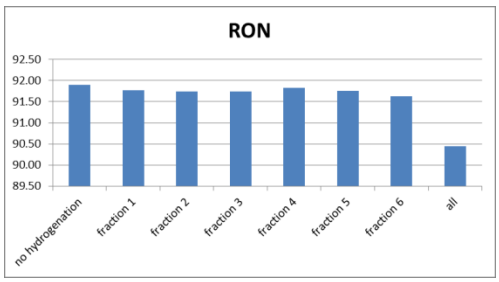
Composition (wt-%) of FCC naphtha 1:

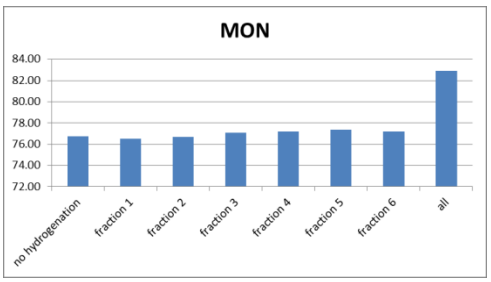
Carbon no.	Naph.	n-paraf.	i-Paraf.	Cyclo-Ol.	Olef.	Arom.	Total
3	-	0.01	-	-	1.94	-	1.96
4	-	0.22	0.04	-	33.21	-	33.48
5	0.47	2.87	22.55	1.54	12.41	-	39.84
6	2.22	0.80	10.76	2.06	1.87	0.81	18.51
7	1.31	0.17	2.29	0.71	0.26	1.07	5.81
8	0.12	-	0.22	0.01	0.01	0.03	0.39
9	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-
11+	-	-	-	-	-	-	-
Total	4.11	4.09	35.86	4.33	49.71	1.90	100.00

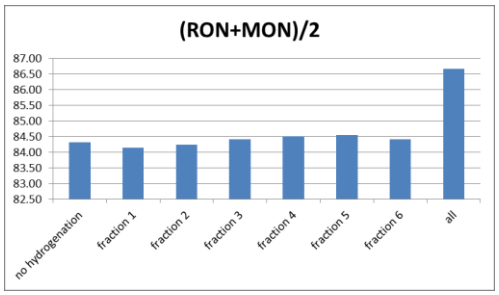
Composition (wt-%) of FCC naphtha 2

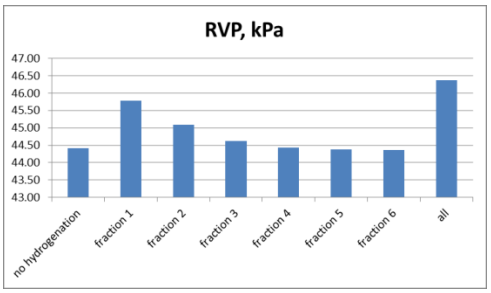
Carbon no.	Naph.	n-paraf.	i-Paraf.	Cyclo-Ol.	Olef.	Arom.	Total
3	-	-	-	-	-	-	-
4	-	0.22	0.05	-	1.66	-	1.92
5	0.12	0.93	5.24	0.43	11.49	-	18.22
6	1.07	0.70	4.53	1.72	9.36	0.38	17.76
7	2.22	0.48	4.06	2.98	7.49	2.22	19.44
8	1.15	0.39	3.03	0.82	7.30	5.19	17.88
9	0.75	0.50	2.71	0.27	5.15	5.87	15.26
10	0.20	0.41	1.92	0.10	4.06	1.54	8.23
11+	0.15	0.03	0.55	-	0.57	-	1.30
Total	5.66	3.66	22.08	6.31	47.08	15.20	100.00

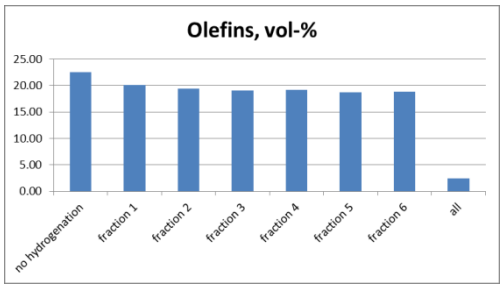
Effect of fraction hydrogenations on synthetic naphtha 1 properties

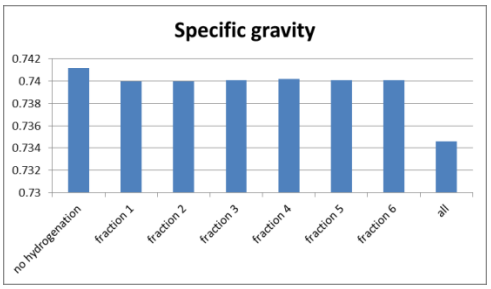






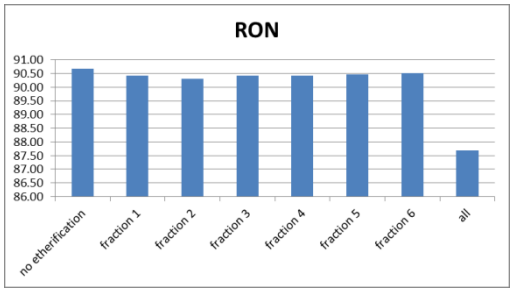


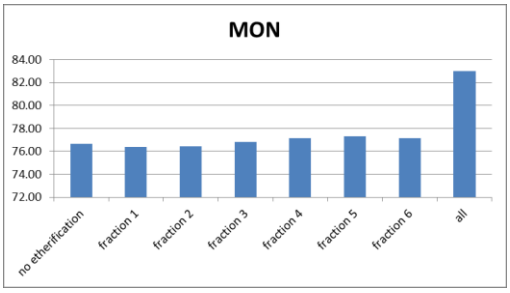


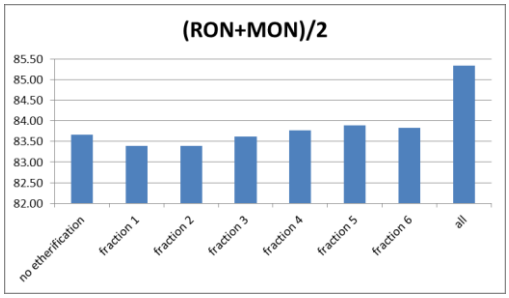


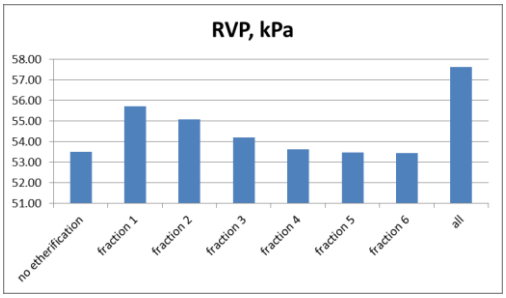
Synthetic Naphtha 1	no hydroge-nation	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	91.90	91.76	91.75	91.74	91.82	91.76	91.62	90.44
MON	76.73	76.50	76.72	77.06	77.20	77.35	77.22	82.89
(RON+MON)/2	84.32	84.13	84.23	84.40	84.51	84.55	84.42	86.67
RVP, kPa	44.42	45.78	45.10	44.62	44.44	44.38	44.37	46.38
Olefins, vol-%	22.57	20.11	19.43	19.11	19.22	18.69	18.88	2.44
Specific gravity	0.7412	0.7400	0.7400	0.7401	0.7402	0.7401	0.7401	0.7346

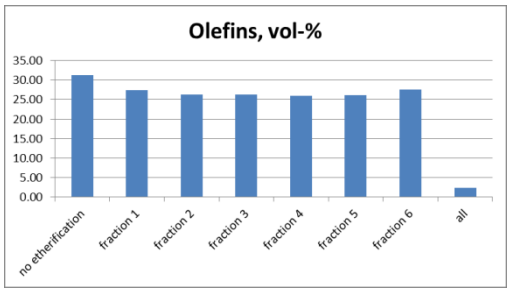
Effect of fraction hydrogenations on synthetic naphtha 2 properties.

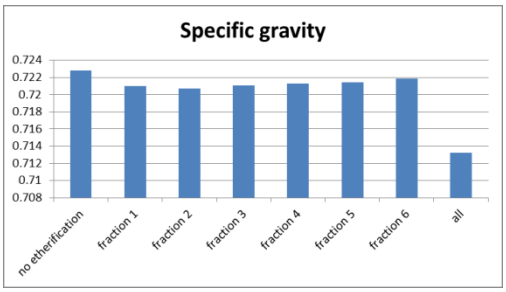






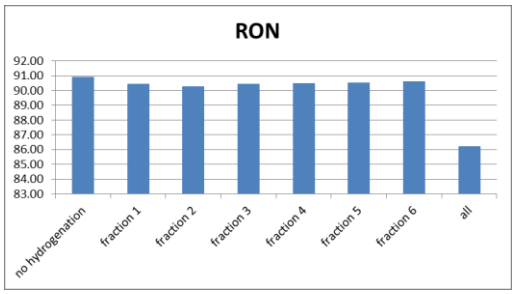


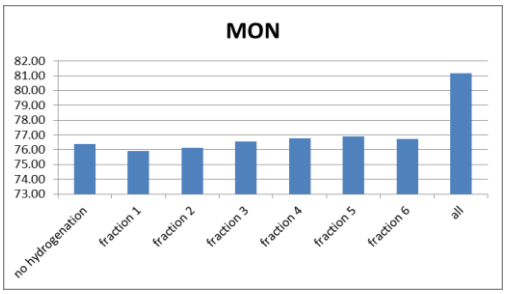


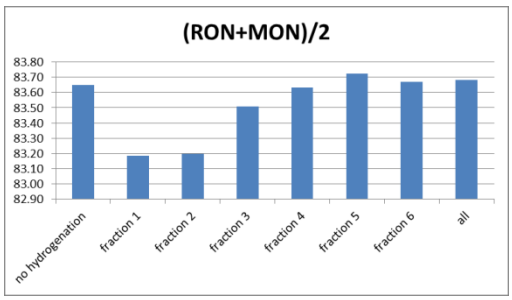


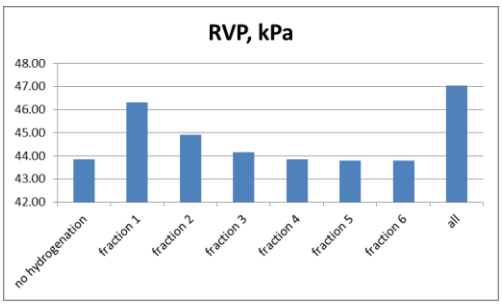
Synthetic Naphtha 2	no hydroge-nation	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	90.68	90.42	90.31	90.41	90.41	90.47	90.52	87.68
MON	76.67	76.36	76.46	76.83	77.14	77.30	77.14	83.01
(RON+MON)/2	83.67	83.39	83.39	83.62	83.78	83.89	83.83	85.34
RVP, kPa	53.49	55.72	55.09	54.21	53.63	53.48	53.44	57.61
Olefins, vol-%	31.19	27.46	26.22	26.28	25.94	26.07	27.63	2.33
Specific gravity	0.7228	0.7210	0.7207	0.7211	0.7213	0.7214	0.7219	0.7132

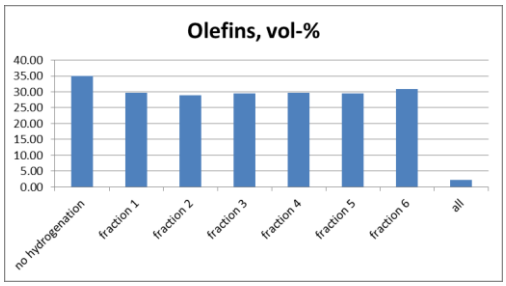
Effect of fraction hydrogenations on synthetic naphtha 3 properties.

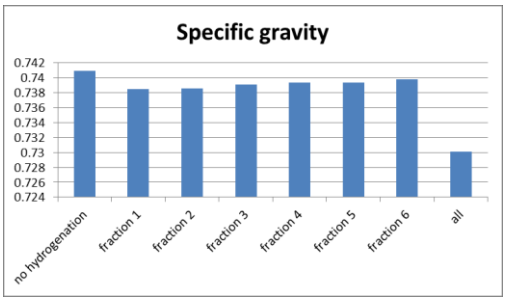






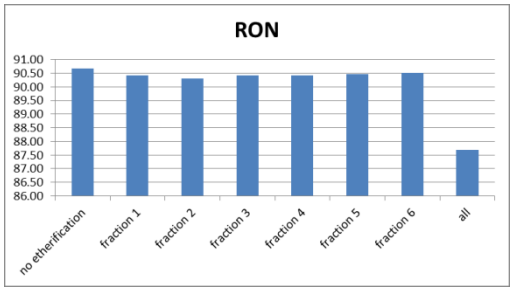


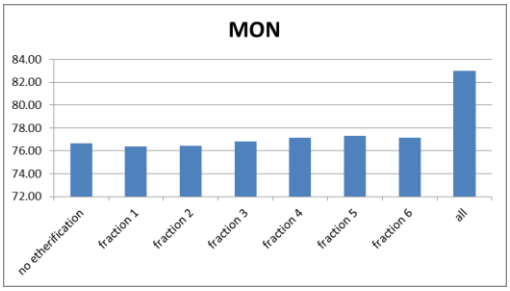


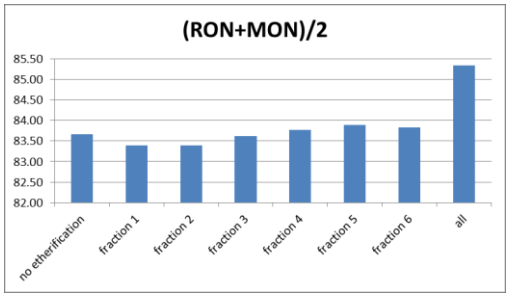


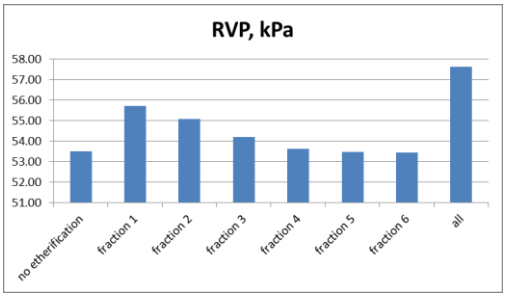
Synthetic Naphtha 3	no hydrogenation	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	90.94	90.46	90.27	90.44	90.51	90.55	90.61	86.21
MON	76.36	75.91	76.13	76.58	76.75	76.90	76.73	81.16
(RON+MON)/2	83.65	83.18	83.20	83.51	83.63	83.73	83.67	83.68
RVP, kPa	43.86	46.32	44.92	44.15	43.86	43.81	43.81	47.03
Olefins, vol-%	35.09	29.69	28.90	29.47	29.66	29.51	30.88	2.29
Specific gravity	0.7409	0.7385	0.7386	0.7391	0.7393	0.7394	0.7397	0.7301

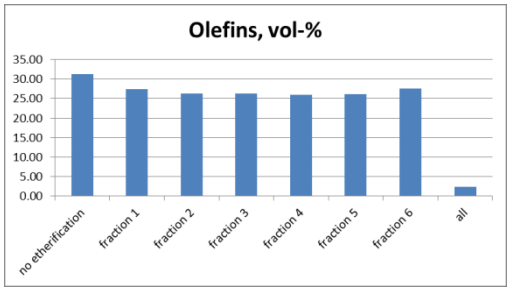
Effect of fraction hydrogenations on synthetic naphtha 4 properties

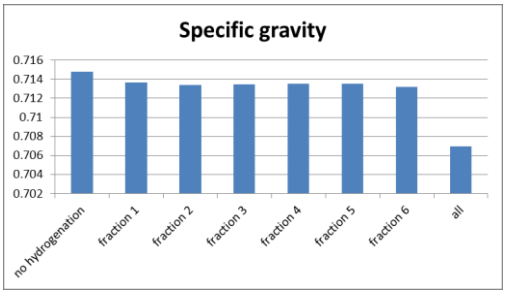






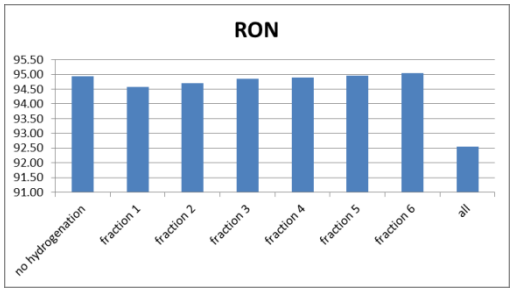


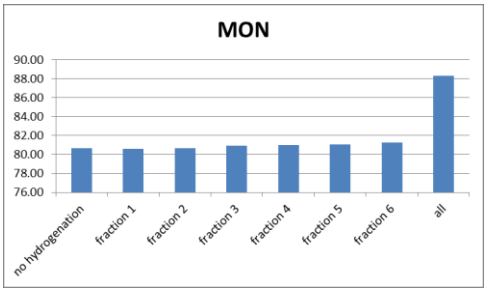


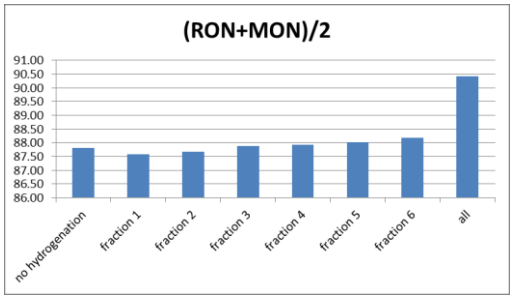


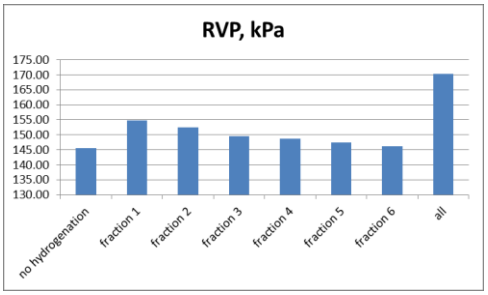
Synthetic Naphtha 4	no hydroge-nation	fractio n 1	fractio n 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	89.39	89.14	89.01	88.92	88.96	88.98	88.69	85.06
MON	76.39	76.14	76.20	76.62	76.73	76.87	77.02	81.79
(RON+MON)/2	82.89	82.64	82.61	82.77	82.84	82.93	82.86	83.43
RVP, kPa	55.79	57.17	56.81	56.12	55.86	55.79	55.71	58.17
Olefins, vol-%	27.08	24.69	23.68	22.81	22.85	22.62	21.40	2.36
Specific gravity	0.7148	0.7136	0.7134	0.7134	0.7135	0.7135	0.7132	0.7070

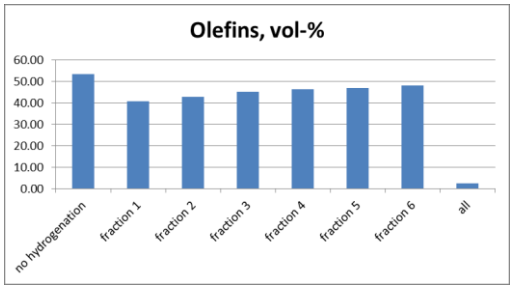
Effect of fraction hydrogenations on FCC naphtha 1 properties

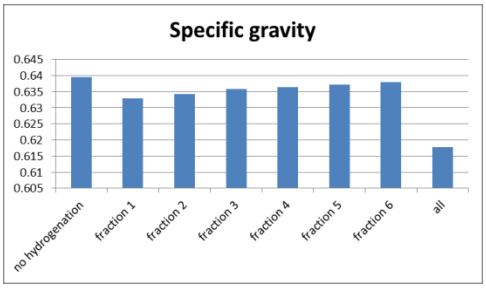






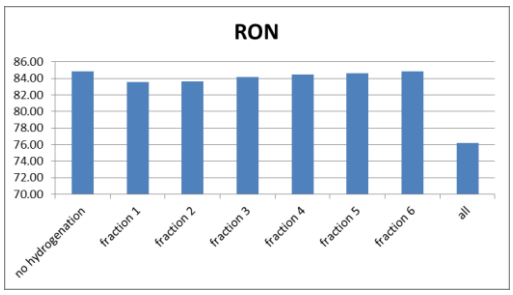


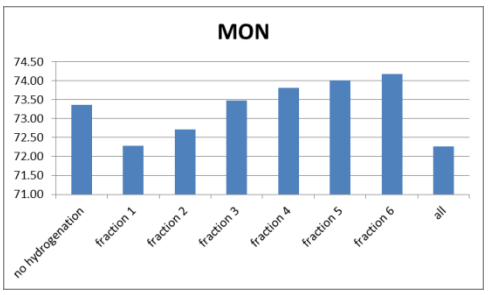


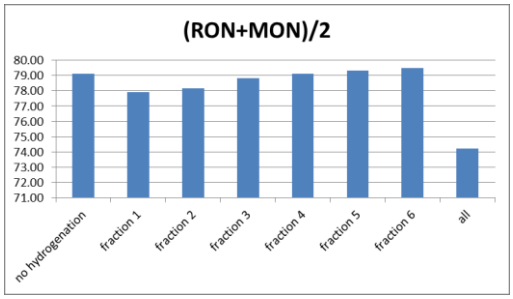


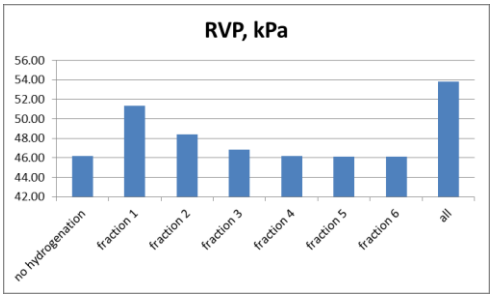
FCC Naphtha 1	no hydroge-nation	fractio n 1	fractio n 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	94.95	94.58	94.70	94.85	94.90	94.96	95.05	92.54
MON	80.68	80.57	80.67	80.93	80.96	81.07	81.29	88.31
(RON+MON)/2	87.82	87.57	87.68	87.89	87.93	88.01	88.17	90.43
RVP, kPa	145.49	154.80	152.49	149.54	148.62	147.44	146.24	170.22
Olefins, vol-%	53.35	40.61	42.89	45.17	46.21	47.00	48.15	2.50
Specific gravity	0.6395	0.6329	0.6343	0.6359	0.6365	0.6371	0.6380	0.6178

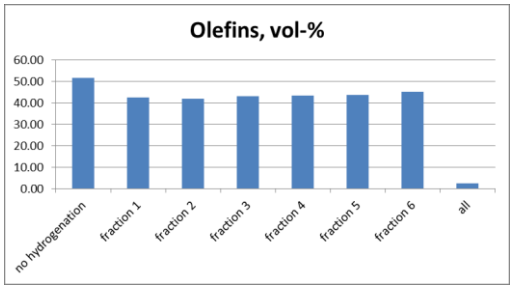
Effect of fraction hydrogenations on FCC naphtha 2 properties

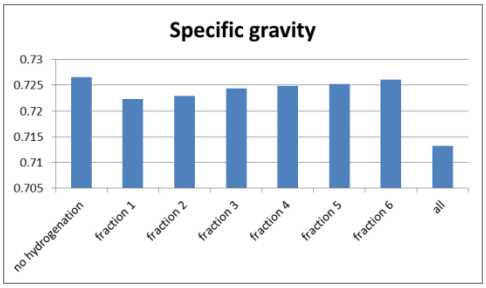






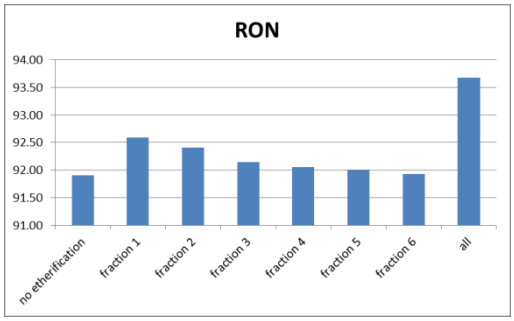


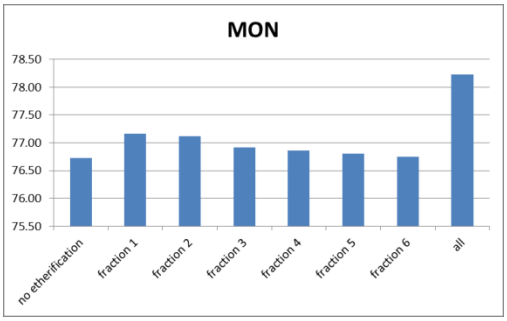


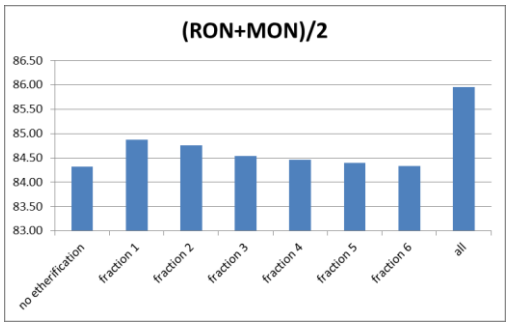


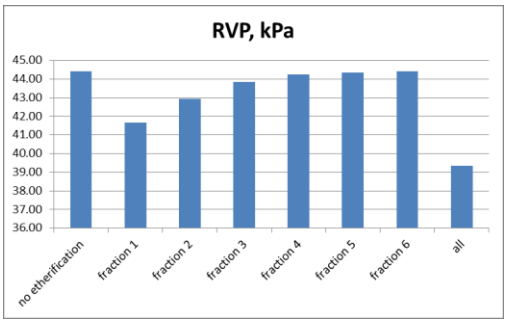
FCC Naphtha 2	no hydroge-nation	fractio n 1	fractio n 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	84.84	83.57	83.59	84.16	84.44	84.62	84.83	76.16
MON	73.37	72.28	72.72	73.47	73.82	74.01	74.18	72.26
(RON+MON)/2	79.10	77.93	78.16	78.82	79.13	79.32	79.51	74.21
RVP, kPa	46.22	51.36	48.40	46.85	46.19	46.11	46.11	53.81
Olefins, vol-%	51.57	42.53	41.97	43.14	43.31	43.81	45.23	2.56
Specific gravity	0.7265	0.7223	0.7230	0.7244	0.7248	0.7252	0.7260	0.7133

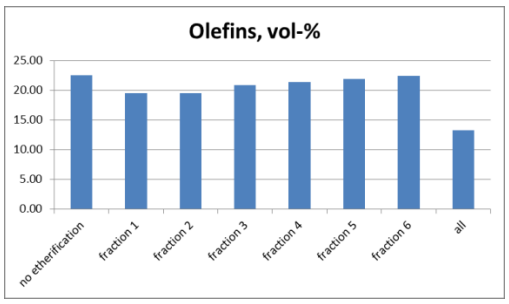
Effect of fraction etherifications on synthetic naphtha 1 properties

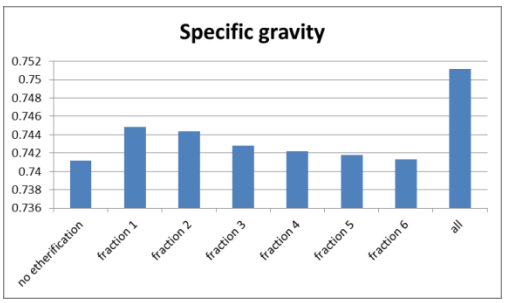


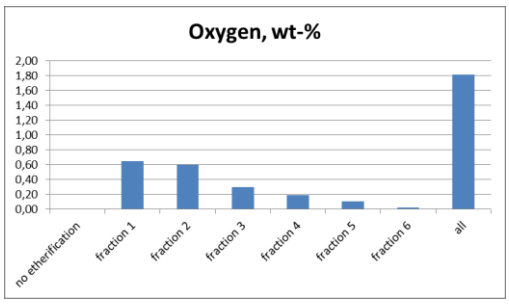






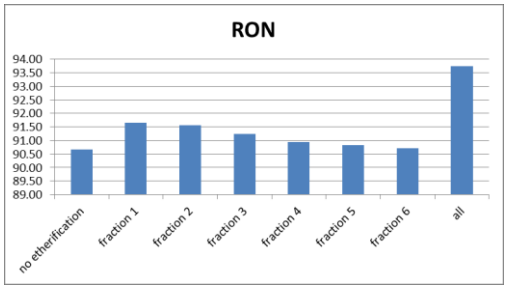


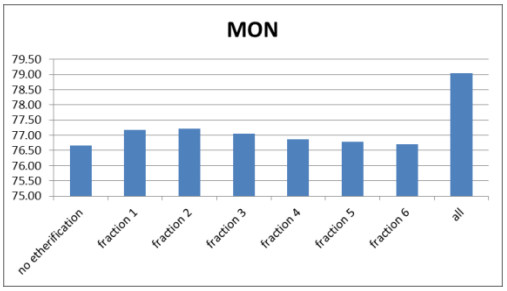


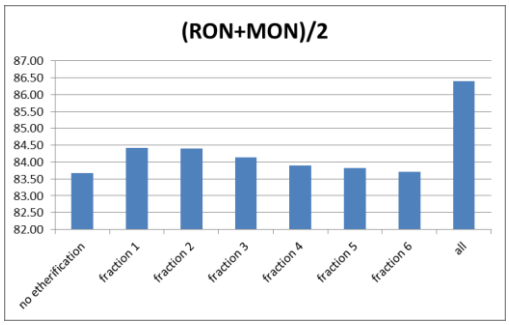


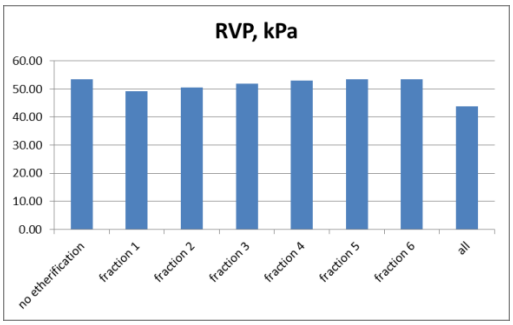
Synthetic Naphtha 1	no etherification	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	91.90	92.59	92.41	92.15	92.06	92.00	91.92	93.67
MON	76.73	77.16	77.11	76.92	76.86	76.81	76.74	78.23
(RON+MON)/2	84.32	84.87	84.76	84.53	84.46	84.40	84.33	85.95
RVP, kPa	44.42	41.65	42.95	43.85	44.26	44.35	44.41	39.34
Olefins, vol-%	22.57	19.60	19.52	20.93	21.41	21.92	22.43	13.33
Specific gravity	0.7412	0.7449	0.7444	0.7428	0.7422	0.7418	0.7413	0.7512
Oxygen, wt-%	0.00	0.65	0.60	0.30	0.19	0.10	0.02	1.82

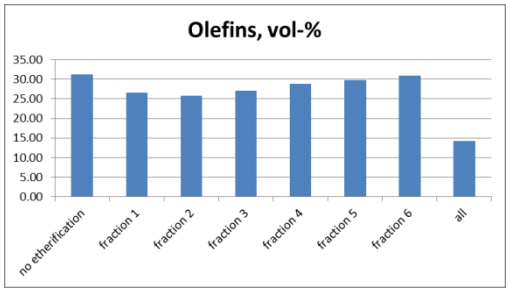
Effect of fraction etherifications on synthetic naphtha 2 properties

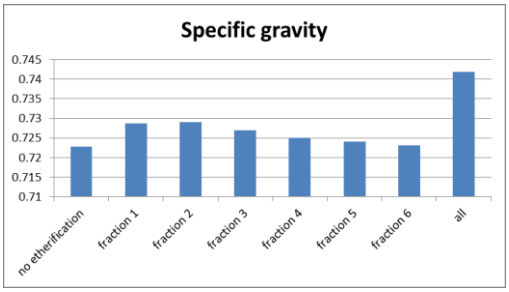


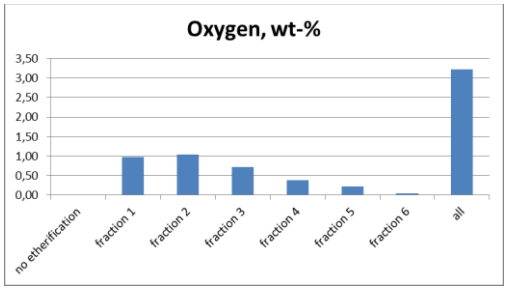






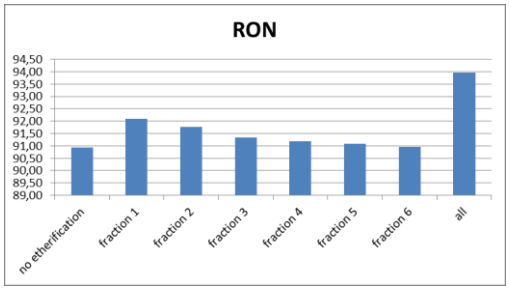


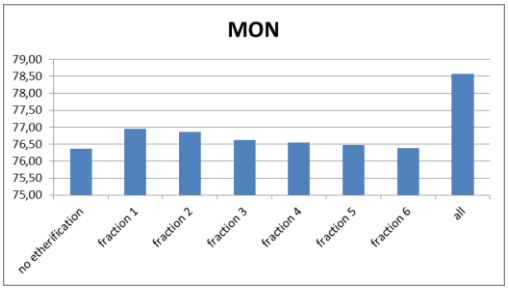


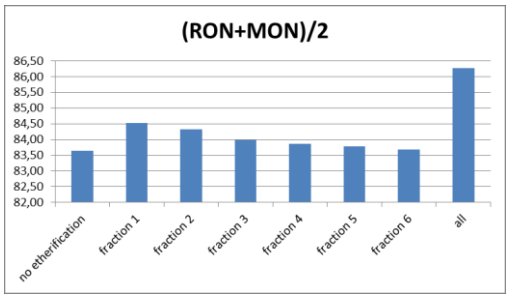


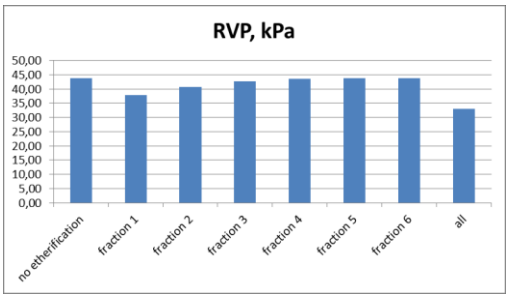
Synthetic Naphtha 2	no etherification	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	90.68	91.64	91.57	91.23	90.94	90.83	90.72	93.75
MON	76.67	77.18	77.22	77.04	76.87	76.79	76.70	79.04
(RON+MON)/2	83.67	84.41	84.39	84.14	83.90	83.81	83.71	86.40
RVP, kPa	53.49	49.13	50.46	51.91	53.06	53.35	53.47	43.79
Olefins, vol-%	31.19	26.54	25.77	27.16	28.86	29.79	30.86	14.24
Specific gravity	0.7228	0.7287	0.7290	0.7270	0.7250	0.7241	0.7231	0.7419
Oxygen, wt-%	0.00	0.97	1.04	0.72	0.38	0.21	0.05	3.22

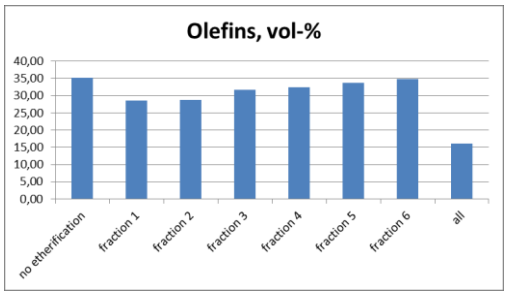
Effect of fraction etherifications on synthetic naphtha 3 properties

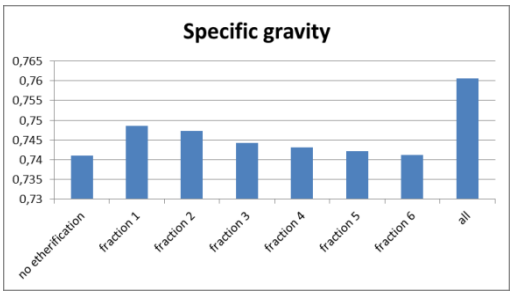


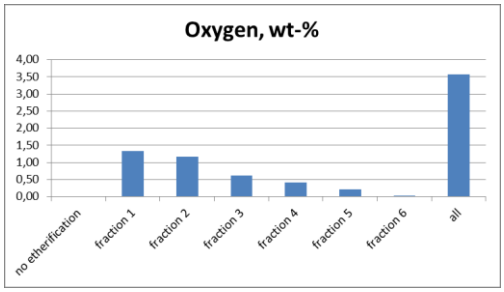






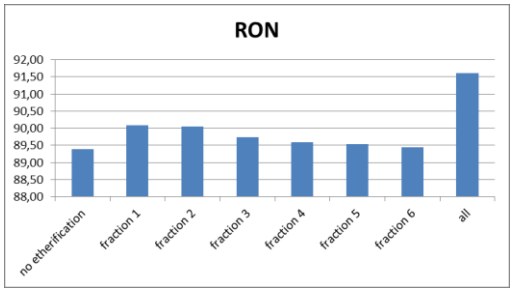


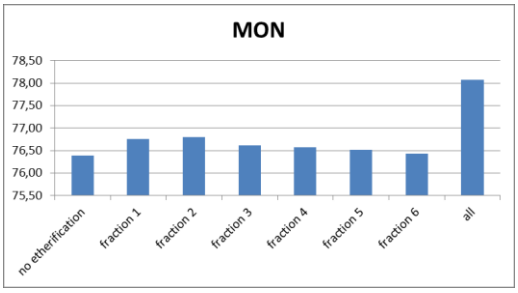


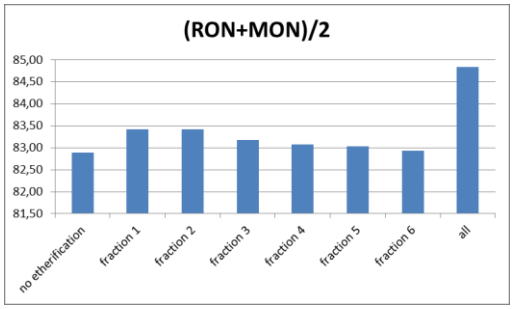


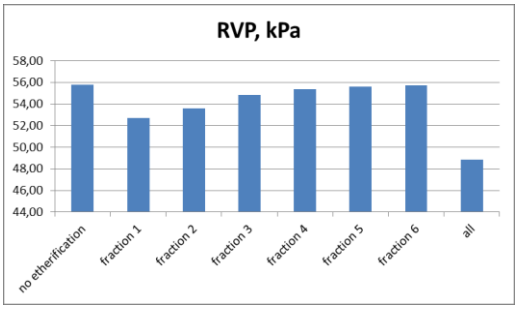
Synthetic Naphtha 3	no etherification	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	90.94	92.10	91.77	91.33	91.19	91.08	90.96	93.96
MON	76.36	76.96	76.87	76.62	76.55	76.47	76.38	78.57
(RON+MON)/2	83.65	84.53	84.32	83.98	83.87	83.77	83.67	86.27
RVP, kPa	43.86	37.91	40.80	42.67	43.50	43.73	43.84	32.94
Olefins, vol-%	35.09	28.61	28.76	31.62	32.49	33.68	34.84	16.04
Specific gravity	0.7409	0.7485	0.7473	0.7442	0.7432	0.7421	0.7412	0.7607
Oxygen, wt-%	0.00	1.33	1.17	0.61	0.41	0.21	0.04	3.58

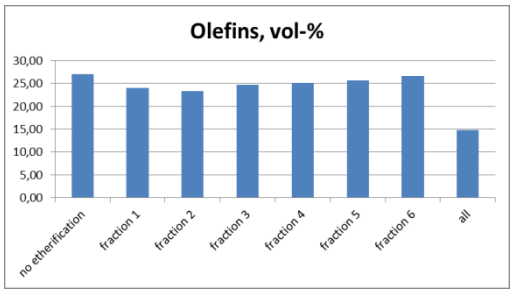
Effect of fraction etherifications on synthetic naphtha 4 properties

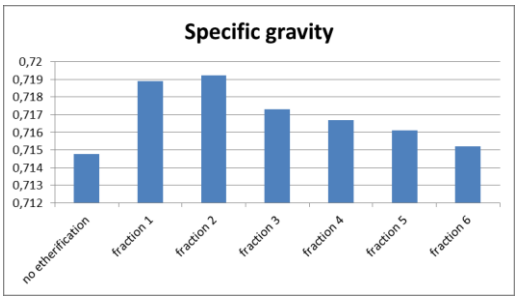


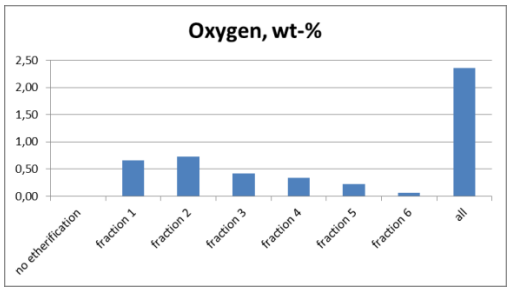






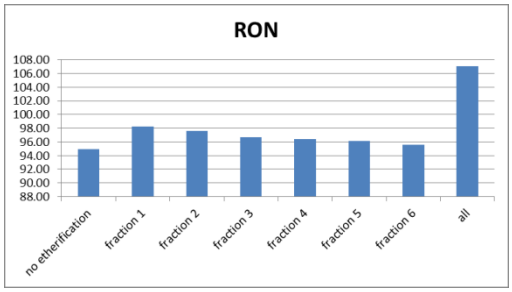


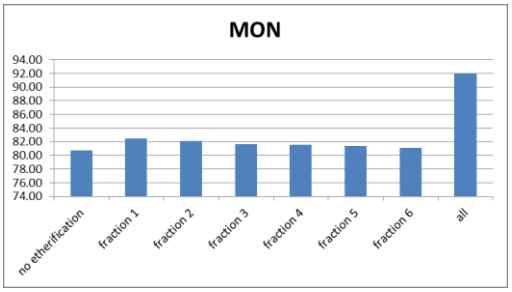


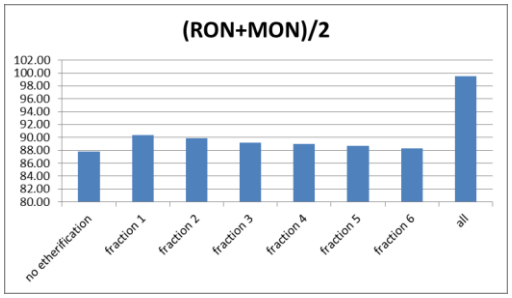


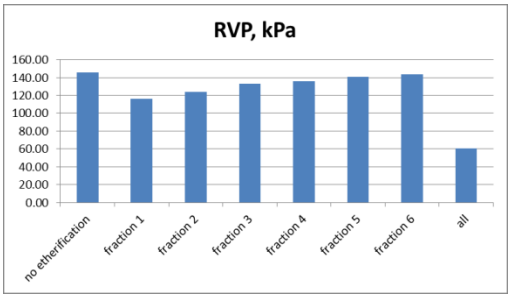
Synthetic Naphtha 4	no etherifi-cation	fractio n 1	fraction 2	fractio n 3	fraction 4	fractio n 5	fraction 6	all
RON	89.39	90.08	90.05	89.73	89.59	89.54	89.44	91.61
MON	76.39	76.76	76.79	76.62	76.56	76.52	76.44	78.06
(RON+MON)/ 2	82.89	83.42	83.42	83.17	83.08	83.03	82.94	84.84
RVP, kPa	55.79	52.70	53.59	54.82	55.39	55.59	55.74	48.86
Olefins, vol-%	27.08	24.00	23.39	24.78	25.09	25.65	26.63	14.78
Specific gravity	0.7148	0.7189	0.7192	0.7173	0.7167	0.7161	0.7152	0.7290
Oxygen, wt-%	0.00	0.66	0.73	0.42	0.33	0.23	0.07	2.35

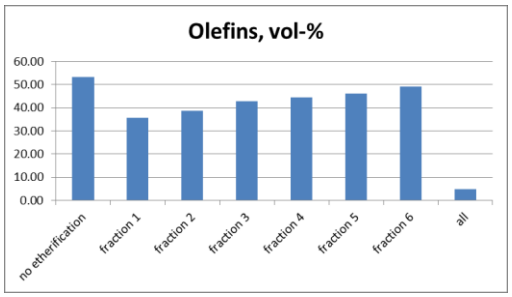
Effect of fraction etherifications on FCC naphtha 1 properties

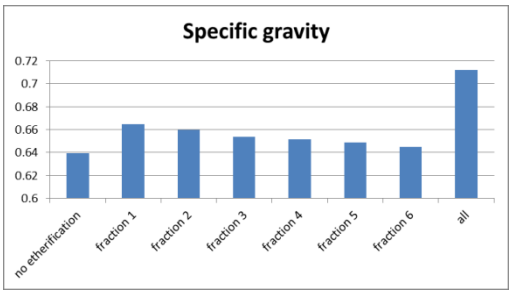


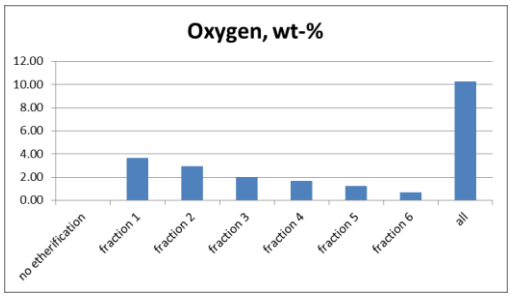






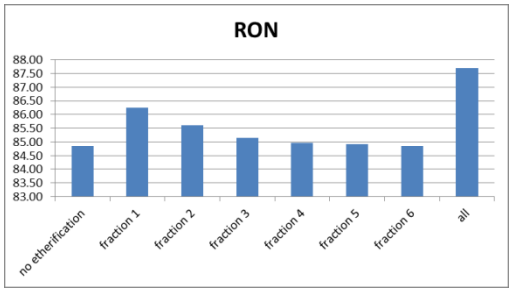


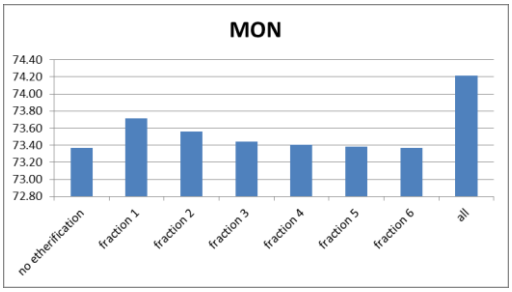


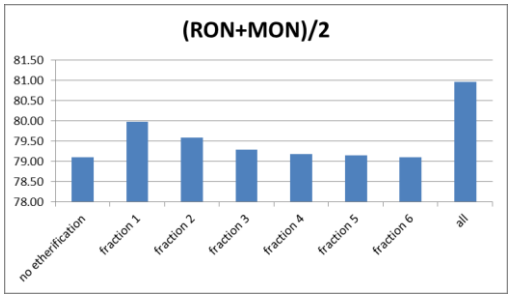


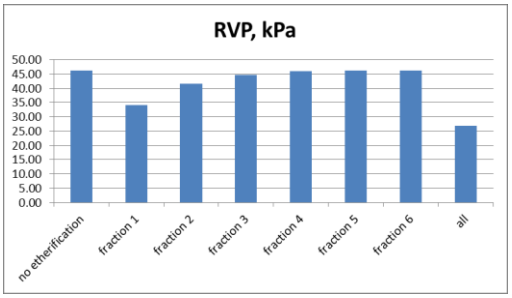
FCC Naphtha 1	no etherification	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	94.95	98.25	97.59	96.72	96.43	96.10	95.54	107.08
MON	80.68	82.50	82.13	81.67	81.52	81.38	81.08	91.94
(RON+MON)/2	87.82	90.38	89.86	89.20	88.97	88.74	88.31	99.51
RVP, kPa	145.49	116.14	123.62	132.74	136.16	140.46	143.88	60.58
Olefins, vol-%	53.35	35.76	38.82	42.94	44.47	46.11	49.11	4.83
Specific gravity	0.6395	0.6647	0.6600	0.6538	0.6515	0.6490	0.6447	0.7120
Oxygen, wt-%	0.00	3.69	2.96	2.02	1.66	1.26	0.68	10.27

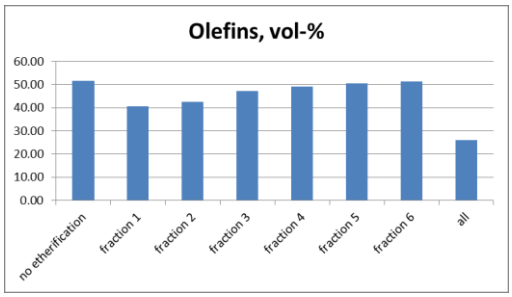
Effect of fraction etherifications on FCC naphtha 2 properties

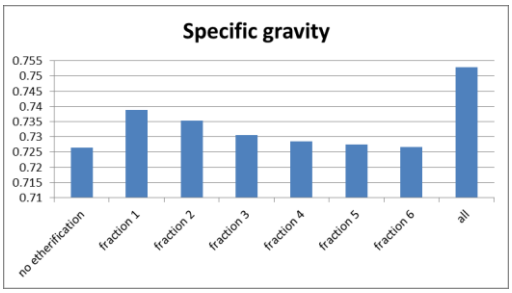


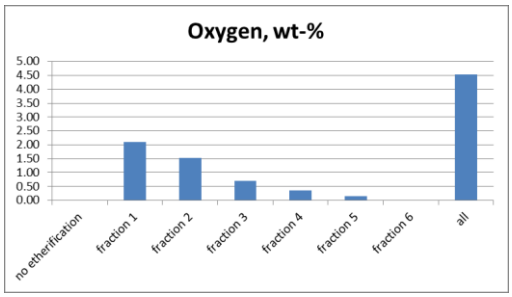










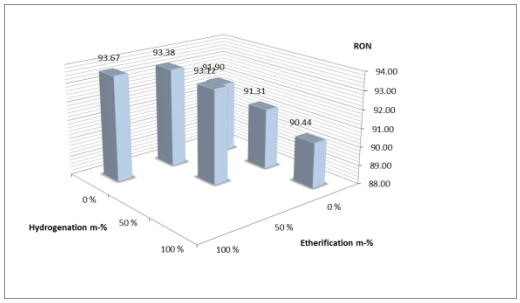


FCC Naphtha 2	no etherification	fraction 1	fraction 2	fraction 3	fraction 4	fraction 5	fraction 6	all
RON	84.84	86.25	85.61	85.15	84.97	84.91	84.86	87.71
MON	73.37	73.71	73.56	73.44	73.40	73.39	73.37	74.21
(RON+MON)/2	79.10	79.98	79.59	79.29	79.19	79.15	79.11	80.96
RVP, kPa	46.22	34.06	41.59	44.64	45.93	46.13	46.21	26.94
Olefins, vol-%	51.57	40.64	42.64	47.26	49.14	50.46	51.39	26.08
Specific gravity	0.7265	0.7388	0.7353	0.7305	0.7285	0.7274	0.7267	0.7529
Oxygen, wt-%	0.00	2.09	1.53	0.70	0.35	0.15	0.02	4.54

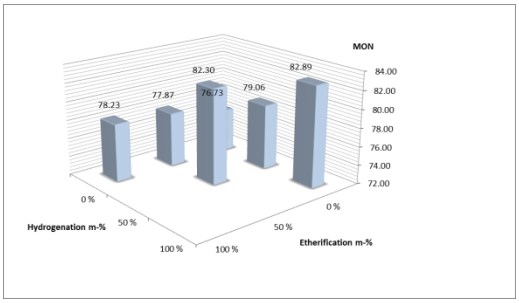
Synthetic Naphtha 1

Effect of Processing Scenarios on Naphtha Properties

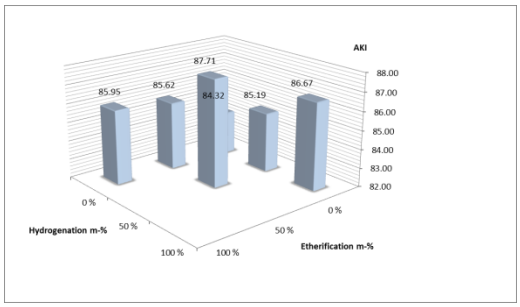
RON



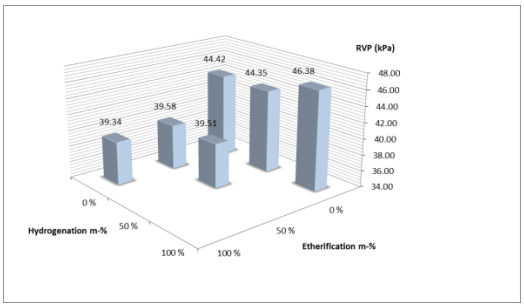
MON



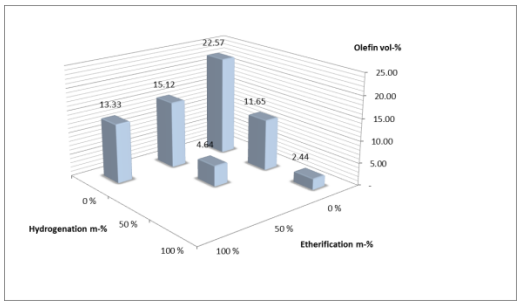
AKI



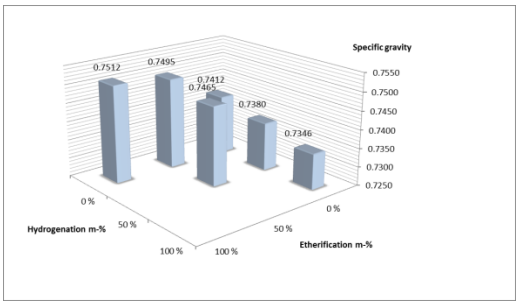
RVP (kPa)



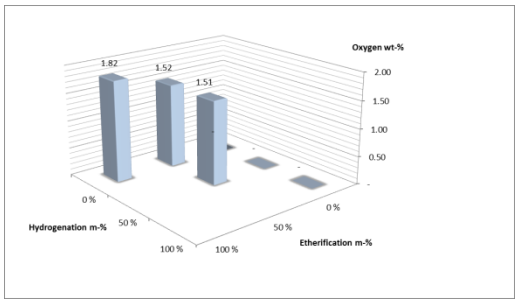
Olefin (vol-%)



Specific gravity



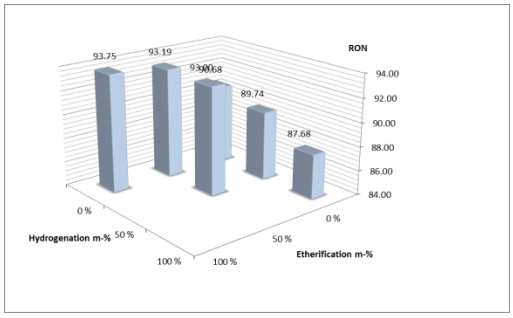
Oxygen (wt-%)



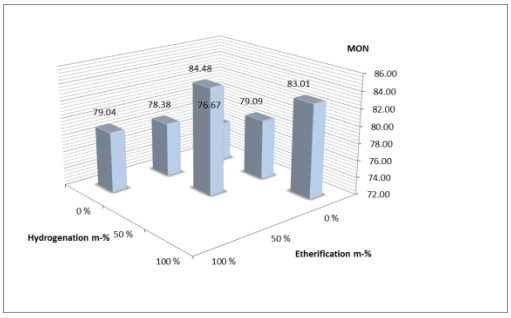
Synthetic Naphtha 2

Effect of Processing Scenarios on Naphtha Properties

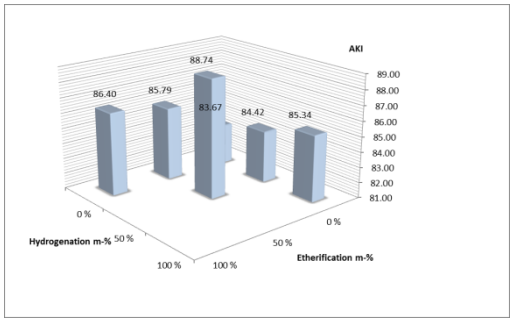
RON



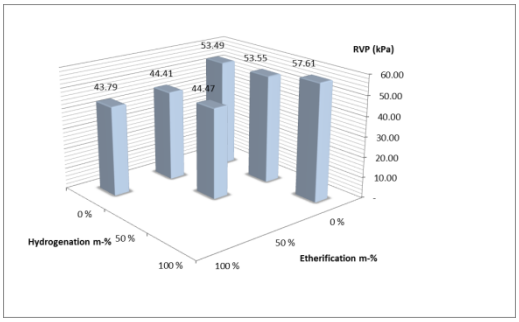
MON



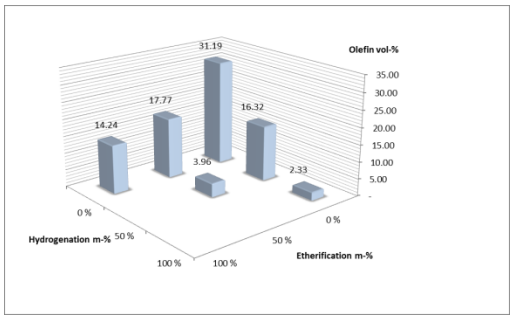
AKI



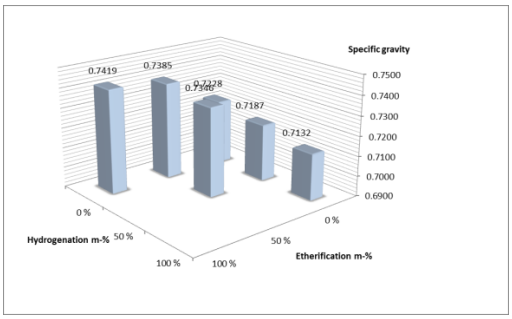
RVP (kPa)



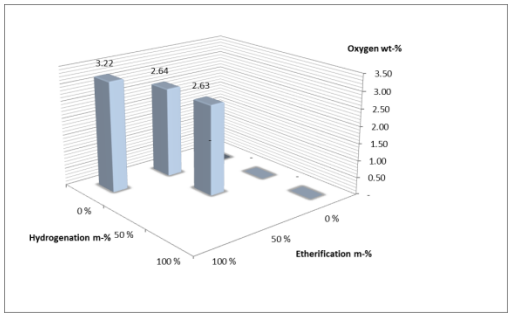
Olefin (vol-%)



Specific gravity



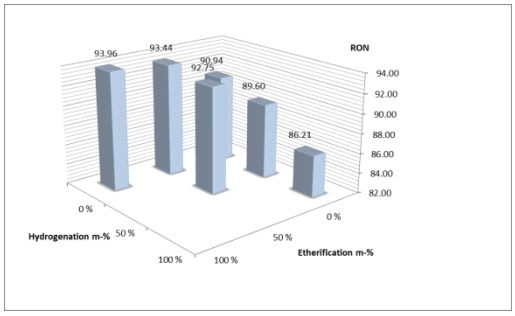
Oxygen (wt-%)



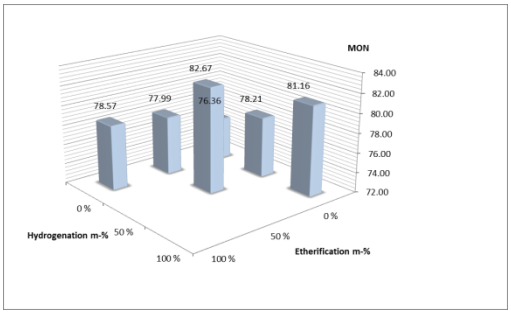
Synthetic Naphtha 3

Effect of Processing Scenarios on Naphtha Properties

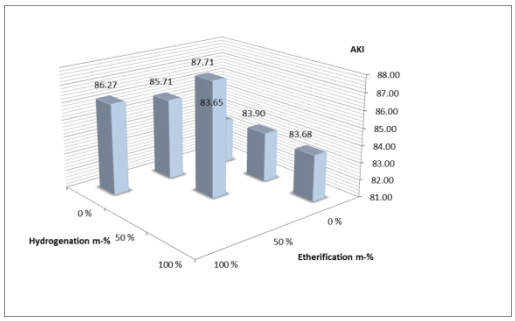
RON



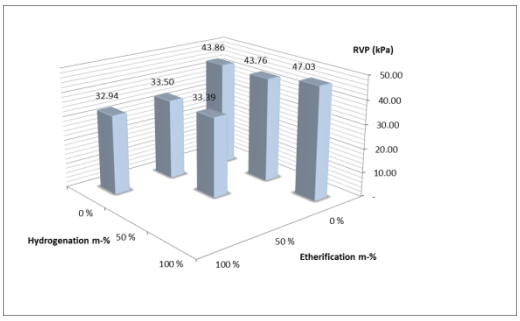
MON



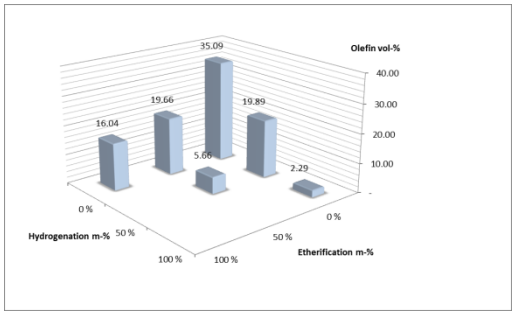
AKI



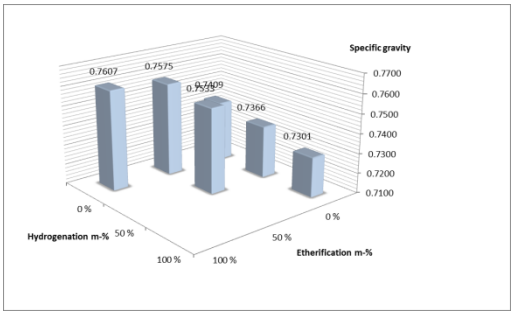
RVP (kPa)



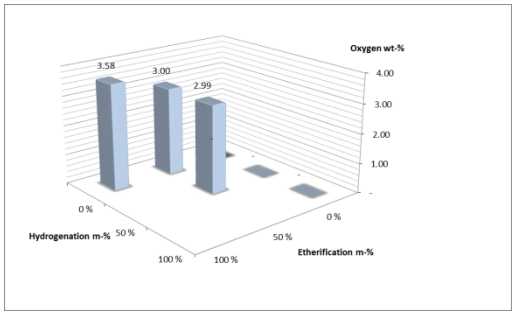
Olefin (vol-%)



Specific gravity



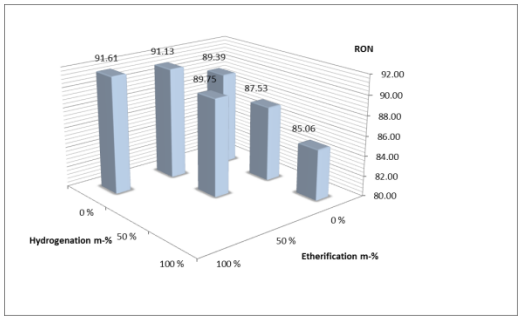
Oxygen (wt-%)



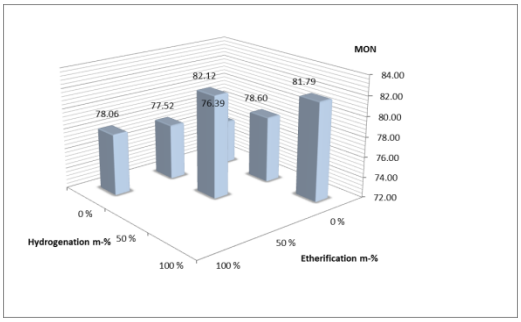
Synthetic Naphtha 4

Effect of Processing Scenarios on Naphtha Properties

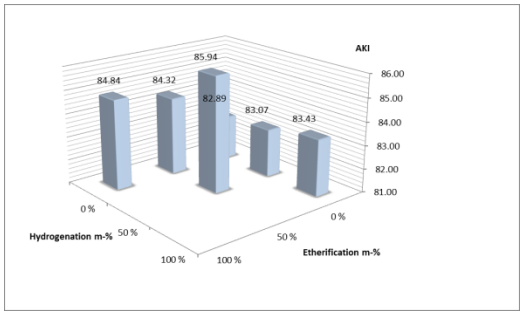
RON



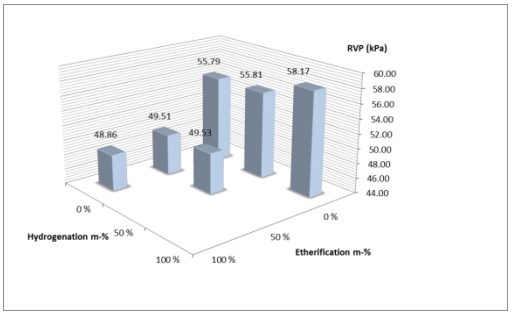
MON



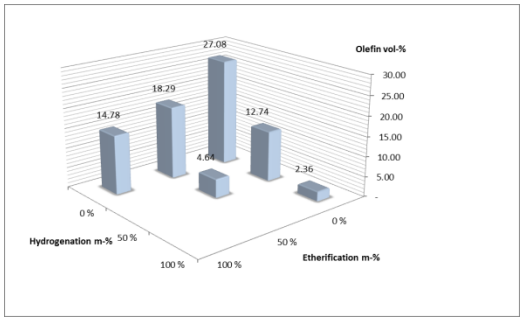
AKI



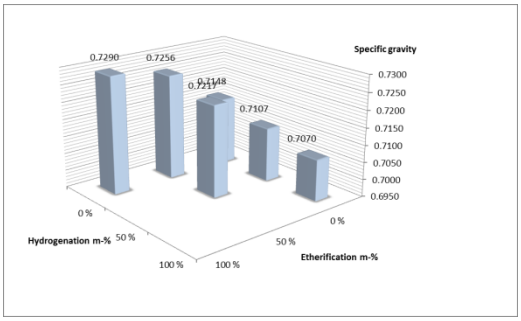
RVP (kPa)



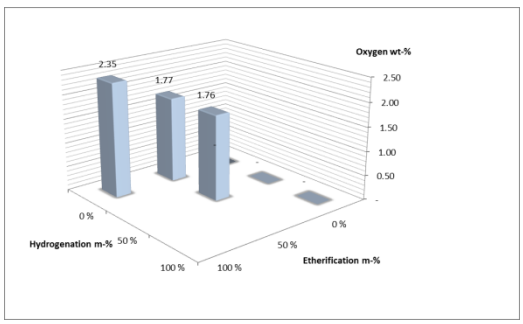
Olefin (vol-%)



Specific gravity



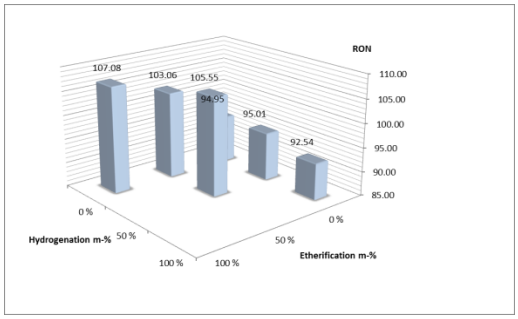
Oxygen (wt-%)



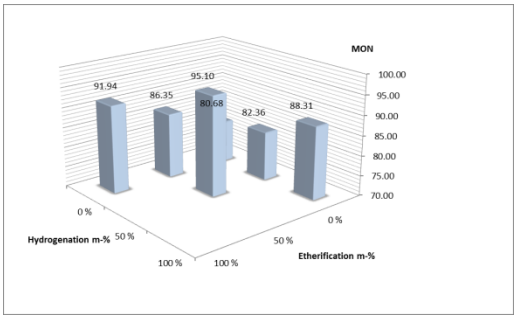
FCC Naphtha 1

Effect of Processing Scenarios on Naphtha Properties

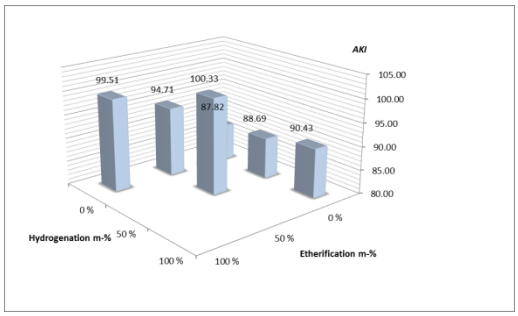
RON



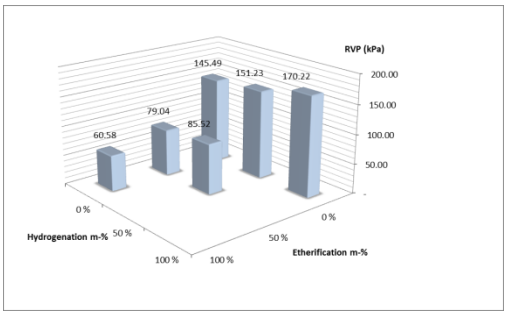
MON



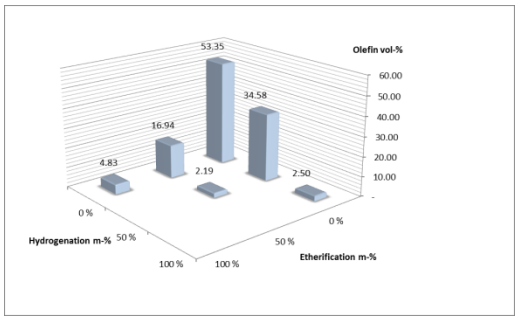
AKI



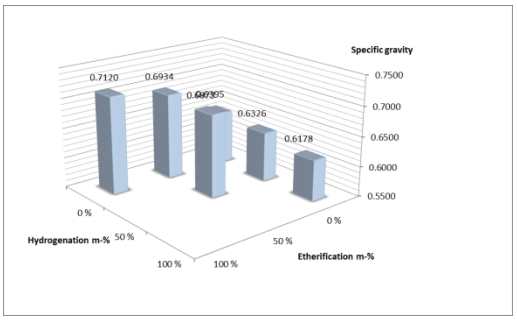
RVP (kPa)



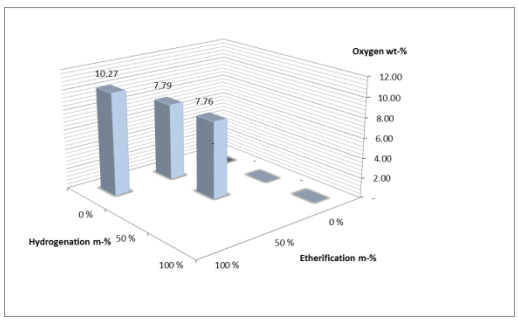
Olefin (vol-%)



Specific gravity



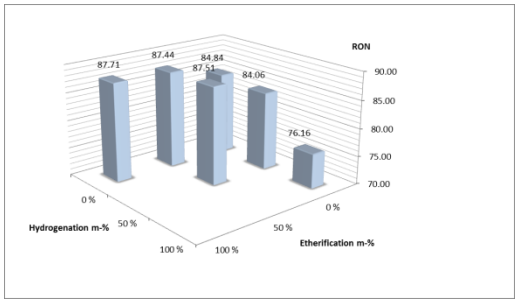
Oxygen (wt-%)



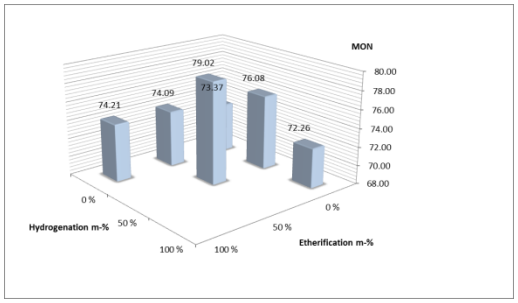
FCC Naphtha 2

Effect of Processing Scenarios on Naphtha Properties

RON



MON



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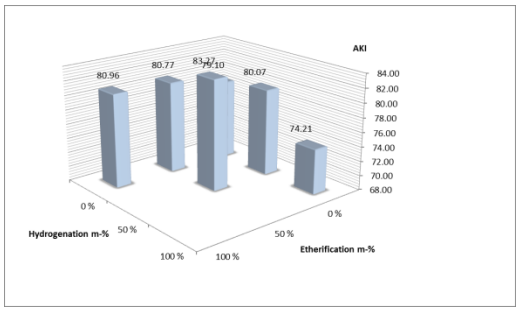
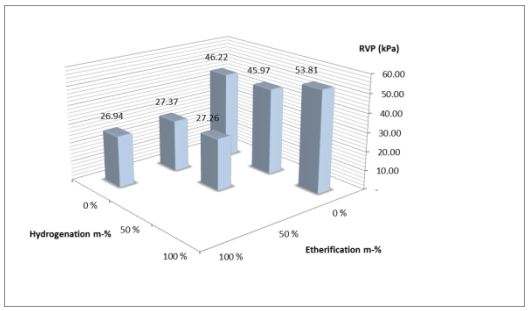
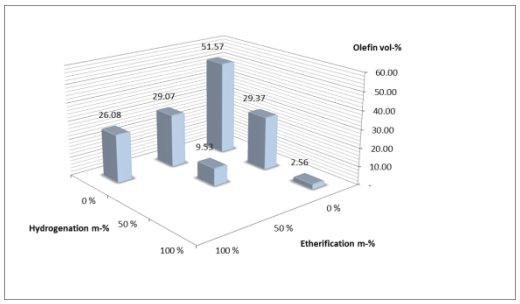


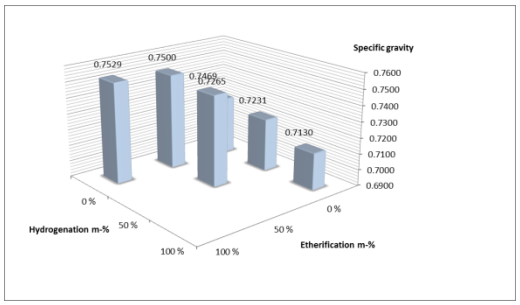
RVP (kPa)



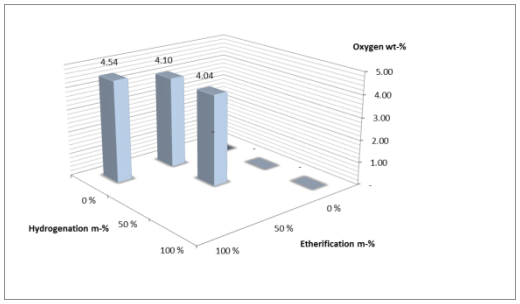
Olefin (vol-%)



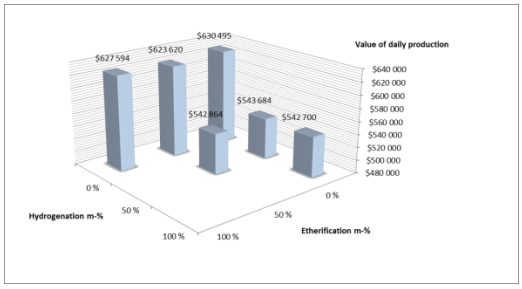
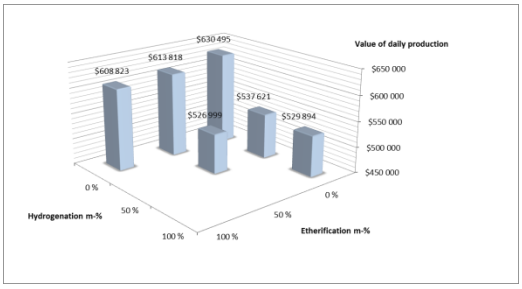
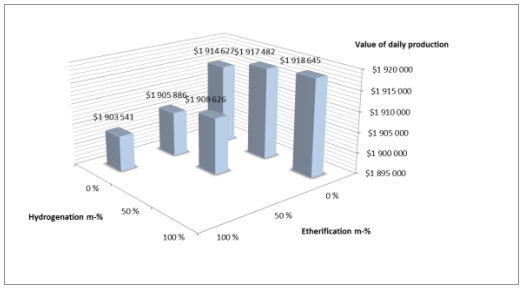
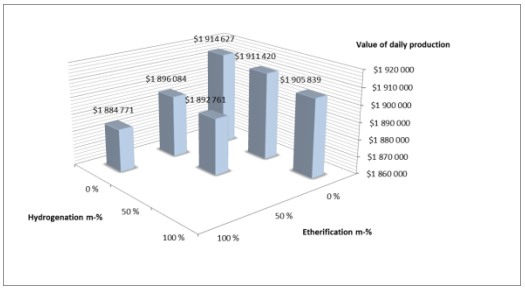
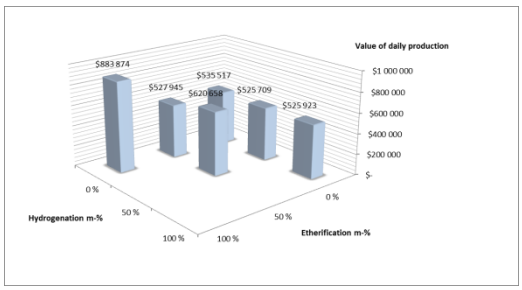
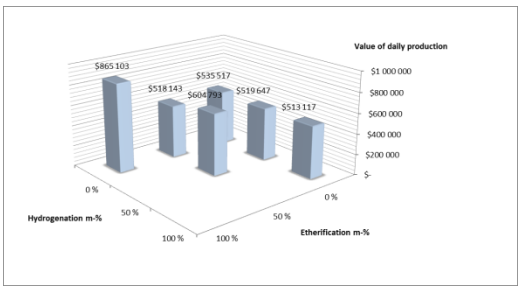
Specific gravity



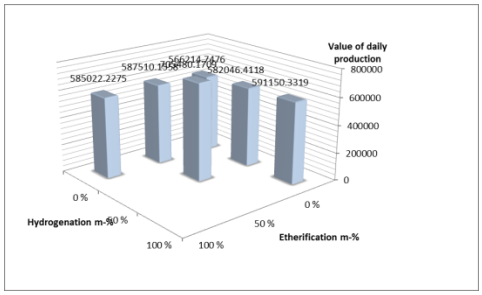
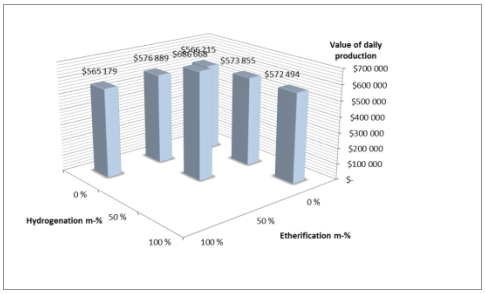
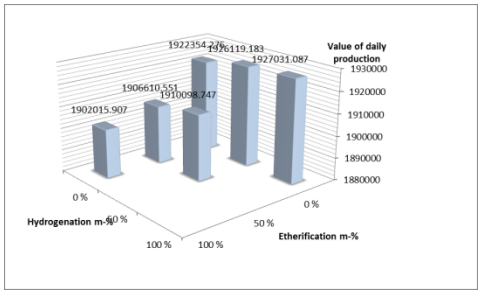
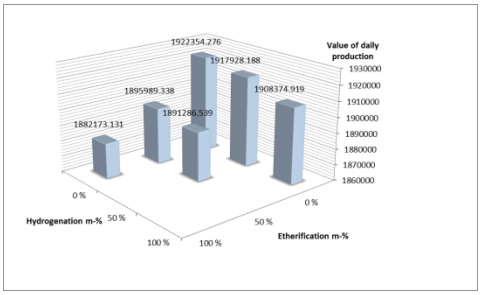
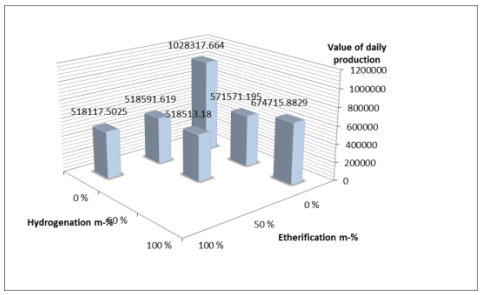
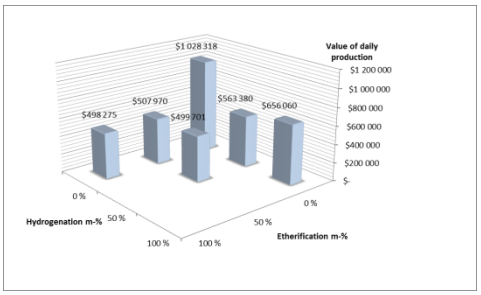
Oxygen (wt-%)



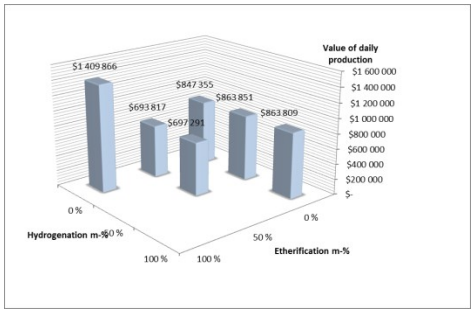
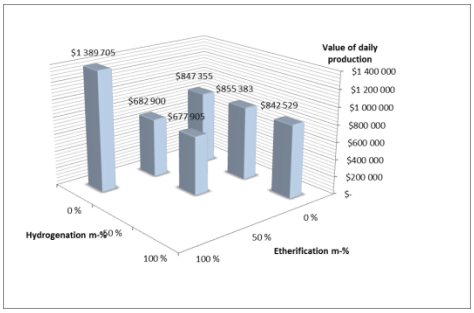
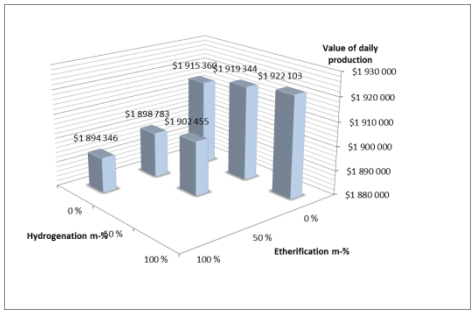
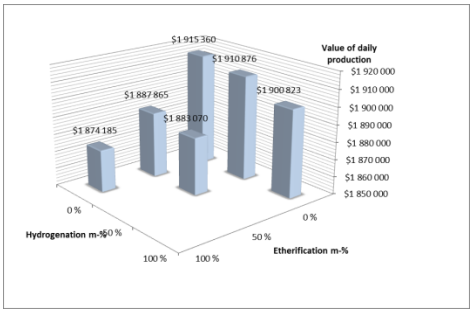
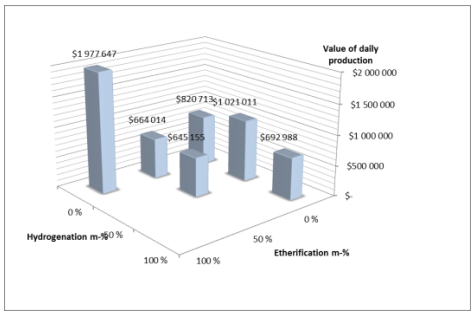
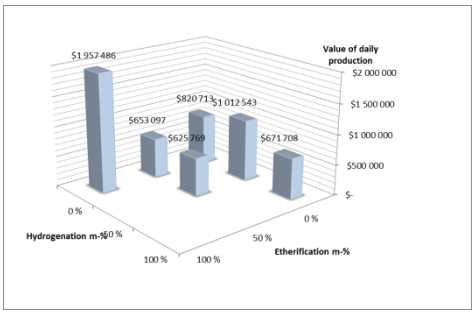
Synthetic Naphtha 1

Profit Without Processing Costs:	Profit With Estimated Processing Costs:
Gulf Coast Refinery	*Gulf Coast Refinery*
	
European Refinery	*European Refinery*
	
Californian Refinery	*Californian Refinery*
	

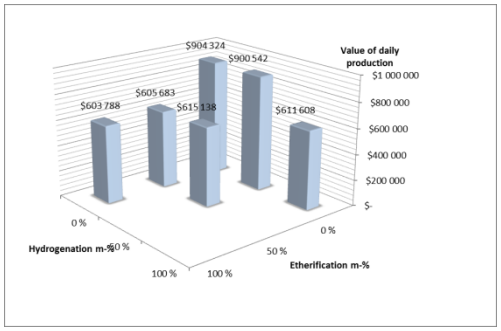
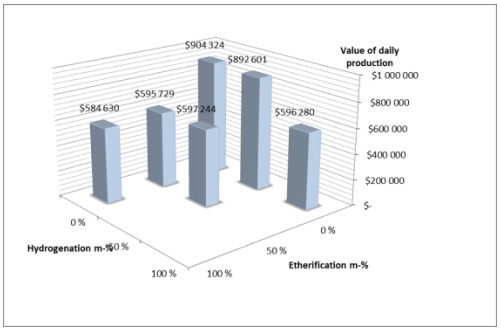
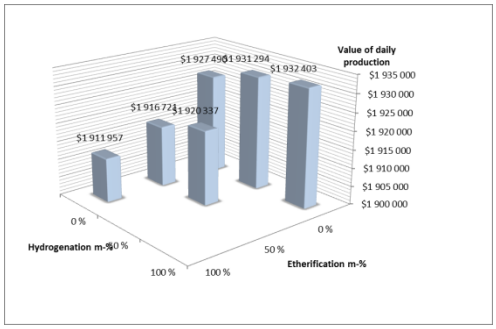
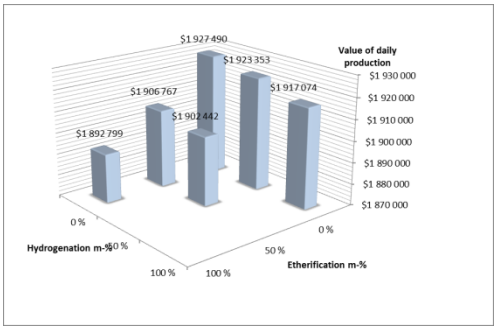
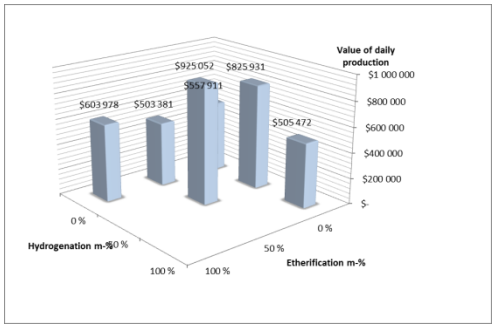
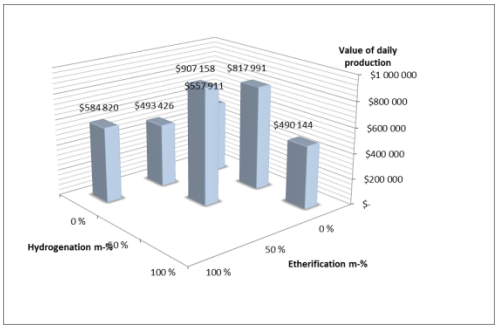
Synthetic Naphtha 2

Profit Without Processing Costs:	Profit With Estimated Processing Costs:
Gulf Coast Refinery	*Gulf Coast Refinery*
	
European Refinery	*European Refinery*
	
Californian Refinery	*Californian Refinery*
	

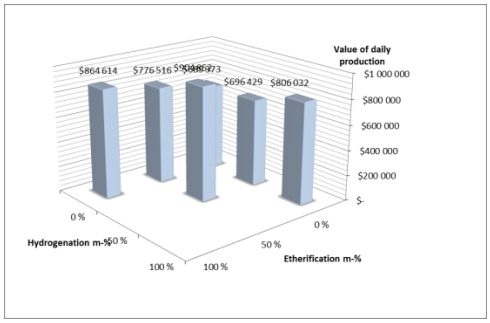
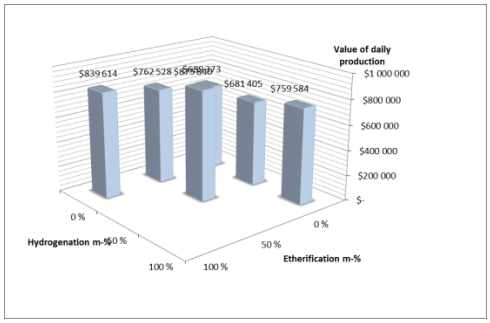
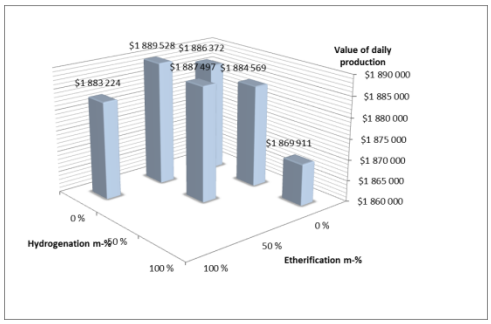
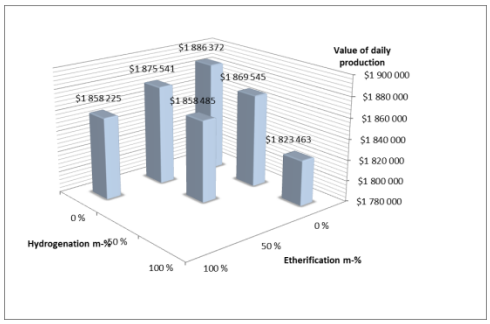
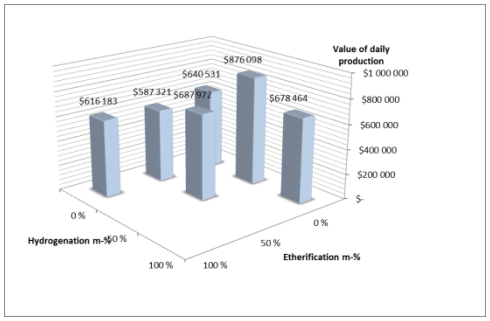
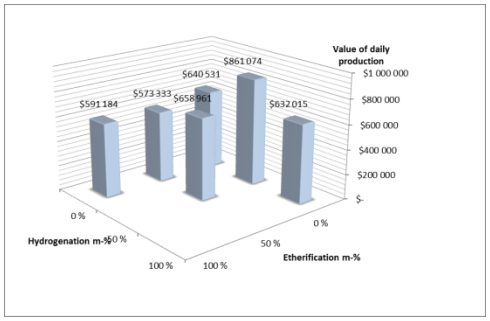
Synthetic Naphtha 3

Profit Without Processing Costs:	Profit With Estimated Processing Costs:
Gulf Coast Refinery	*Gulf Coast Refinery*
	
European Refinery	*European Refinery*
	
Californian Refinery	*Californian Refinery*
	

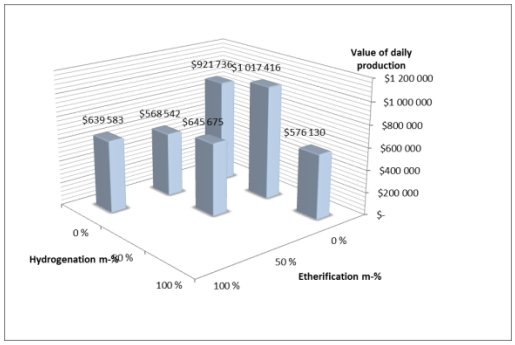
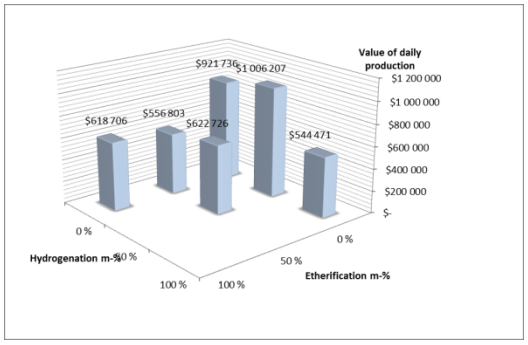
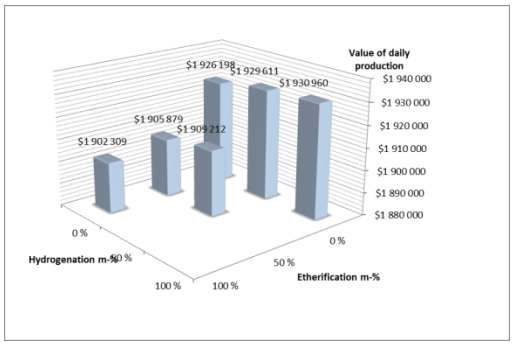
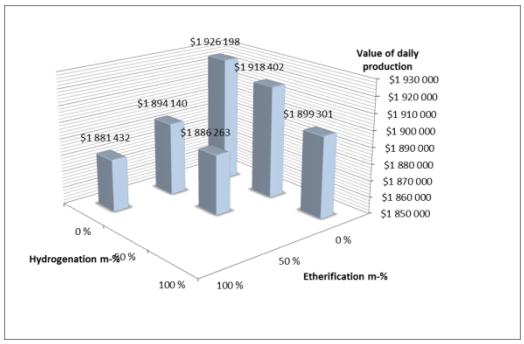
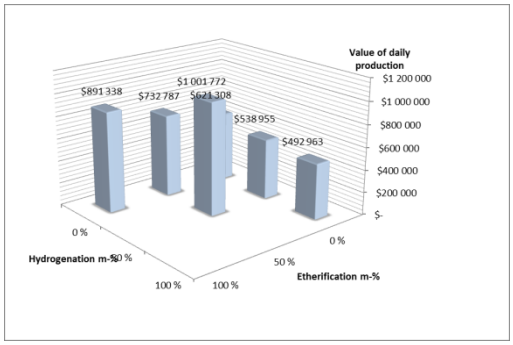
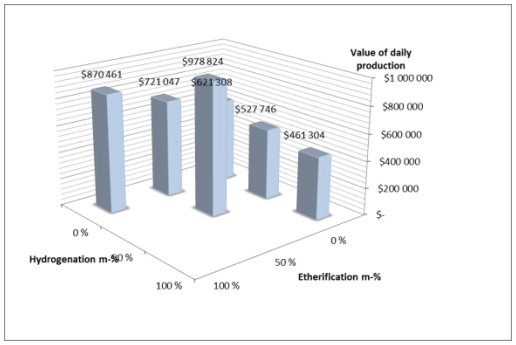
Synthetic Naphtha 4

Profit Without Processing Costs:	Profit With Estimated Processing Costs:
Gulf Coast Refinery	*Gulf Coast Refinery*
	
European Refinery	*European Refinery*
	
Californian Refinery	*Californian Refinery*
	

FCC Naphtha 1

Profit Without Processing Costs:	Profit With Estimated Processing Costs:
Gulf Coast Refinery	*Gulf Coast Refinery*
	
European Refinery	*European Refinery*
	
Californian Refinery	*Californian Refinery*
	

FCC Naphtha 2

Profit Without Processing Costs:	Profit With Estimated Processing Costs:
Gulf Coast Refinery	*Gulf Coast Refinery*
	
European Refinery	*European Refinery*
	
Californian Refinery	*Californian Refinery*
	

APPENDIX 11

Profitability of investment

Processing scenario	Naphtha	Case	Increase in profit per year after processing costs	Investment cost	NPV
PS2	syn1	Colonial pipeline Grade H	-$2 251 361	$6 475 000	-$70 661 086
	syn1	California Refinery	-$5 684 069	$6 475 000	-$127 760 181
	syn2	Colonial pipeline Grade H	-$2 996 352	$6 475 000	-$16 755 294
	syn2	Gulf Coast Refinery	$2 544 734	$6 475 000	$4 272 628
	syn3	Colonial pipeline Grade H	-$3 093 486	$6 475 000	-$17 123 909
	syn4	Colonial pipeline Grade H	-$2 908 642	$6 475 000	-$16 422 444
	fcc1	Gulf Coast Refinery	-$2 918 147	$6 475 000	-$16 458 517
	fcc2	Colonial pipeline Grade H	-$4 052 759	$6 475 000	-$20 764 267
	fcc2	California Refinery	-$32 876 095	$6 475 000	-$130 146 235
PS3	syn1	Colonial pipeline Grade H	-$4 672 105	$9 500 000	-$25 630 125
	syn1	California Refinery	-$8 030 002	$9 500 000	-$38 373 042
	syn2	Colonial pipeline Grade H	-$6 719 938	$9 500 000	-$33 401 465
	syn2	Gulf Coast Refinery	$2 007 796	$9 500 000	-$280 502
	syn3	Colonial pipeline Grade H	-$7 638 075	$9 500 000	-$36 885 715
	syn4	Colonial pipeline Grade H	-$5 554 938	$9 500 000	-$28 980 397
	fcc1	Gulf Coast Refinery	$24 383 725	$9 500 000	$84 634 140
	fcc2	Colonial pipeline Grade H	-$11 270 682	$9 500 000	-$50 671 132
	fcc2	California Refinery	-$56 191 214	$9 500 000	-$221 140 512
PS4	syn1	California Refinery	-$6 420 846	$17 000 000	-$38 503 207
	syn2	Gulf Coast Refinery	$3 395 968	$17 000 000	-$1 249 279
	fcc1	Gulf Coast Refinery	$25 264 419	$17 000 000	$81 739 525
	fcc2	California Refinery	$34 568 843	$17 000 000	$117 048 980
PS5	syn1	California Refinery	$114 855 176	$25 000 000	$415 075 845
	syn2	Gulf Coast Refinery	-$862 353	$25 000 000	-$24 061 778
	fcc1	Gulf Coast Refinery	$52 084 538	$25 000 000	$176 866 917
	fcc2	California Refinery	$86 703 671	$25 000 000	$308 243 414
PS6	syn1	California Refinery	$23 777 081	$23 475 000	$70 710 803
	syn2	Gulf Coast Refinery	$41 689 125	$23 475 000	$138 685 401
	fcc1	Gulf Coast Refinery	$64 794 134	$23 475 000	$226 366 831
	fcc2	California Refinery	$124 661 027	$23 475 000	$453 556 310